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THE EFFECT OF RECOMBINATION
RATE ON THE FLOW OF A
DISSOCIATING DIATOMIC GAS

By

Thomas P. Anderson
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Northwestern University
Evanston, Illinois

September 1961

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ABSTRACT

The flow of a chemically reacting gas through a divergent nozzle is considered. A pure diatomic gas is assumed to dissociate and recombine according to seven distinct recombination rate laws. The effect of correcting Lighthill's "ideal dissociating gas" for vibrational contributions of the molecular species and translational contributions of the atomic species is shown to be small. The effect of recombination rate on the flow of oxygen, from throat conditions of 2 atm and 4050 K, is shown to be significant for reaction rates decreasing with temperature and relatively unimportant for reaction rates increasing with temperature. Electronic analog computer solutions are presented for a variety of throat compositions and recombination rates.

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I. INTRODUCTION

A. Previous Work

Demands for improving the performance of chemical rockets necessitate the use of high energy propellants with resulting higher temperature exhaust products. The analysis of these high energy flow streams becomes increasingly more difficult as the temperature is raised, since real gas effects become more pronounced and there is significant deviation from the classical ideal gas behavior. Thermal phenomena relating to the vibrational and electronic energy levels as well as chemical phenomena relating to the dissociation and the ionisation of the different species must be considered. The rate of change of the various flow parameters must be critically examined to determine whether or not equilibrium has been reached, and even moderate changes such as might be found in the expansion of a pure gas through a hypersonic nozzle often result in non equilibrium flow conditions. These non equilibrium flows are particularly important for several reasons. In order to examine the problem of aerodynamic heating of re-entry vehicles, the flow conditions of the air passing through the bow shock must be known. Also, non equilibrium flows must be generated in test facilities to simulate these re-entry conditions. The thrust of a rocket engine is seriously affected by the extent to which the propellant is dissociated at the nozzle exit and consequently how efficient the engine has been in converting the chemical energy to kinetic energy.

Eggers (Reference 1)* was among the first to correct ideal gases to compensate for real gas effects. He used Berthelot's equation of state to account for the molecular size and intermolecular forces as well as a Planck term to give changes in the vibrational heat capacities. He then analyzed a number of one dimensional flows of a diatomic gas, finding that these imperfect gas corrections became significant for temperatures corresponding to the flow through a shock wave at a Mach number of 10. Chemical reactions were not considered.

The problem of a chemically reacting gas flowing through a nozzle has been examined by Edse (Reference 2). In this study, the gases were assumed to be in a state of perfect thermodynamic and chemical equilibrium at all times and an effective isentropic exponent was defined for the reacting mixture. Equilibrium real gas effects have also been considered by Erickson and Creekmore (Reference 3) and King (Reference 4). Erickson has examined the flow of air and presents a number of charts for the equilibrium properties. King has studied the theoretical performance for an equilibrium mixture of normal hydrogen during an isentropic expansion. Waiter (Reference 5) has included heat addition to a reacting flow with the hypothesis that the flow is in thermodynamic equilibrium at every point.

A linearized treatment of reacting nozzle flow is given by Penner (References 6 and 7). This approximate analysis is then applied to the two extreme cases of very fast reactions, near equilibrium

* References are listed in the Bibliography, Appendix A.

flow, and very slow reactions, near frozen flow. Heims (Reference 8) presents a discussion of the various theories concerning the oxygen recombination rate and also an approximate solution for one dimensional channel flow. Detailed exact numerical solutions are presented by Bray (Reference 9). He considered a Lighthill "ideal dissociating gas" and solved several specific cases as well as presenting an approximate method for the solution of the set of governing equations. In all except one case he assumed the recombination rate was essentially constant. Later Bray (Reference 10) continued these studies and, although he discussed the temperature dependence of the recombination rate, continues to use a constant rate for most of his calculations (this greatly simplifies the already complicated analysis). Freeman (Reference 11) has pointed out that this assumption is doubtful but has presented only semi conclusive arguments. In his later paper Bray also considers the effect of nozzle contour upon the deviation from equilibrium composition. He concluded from his approximate calculations that there are nozzle contours that will have a tendency to keep the composition close to equilibrium but, in general, they are quite long and therefore impractical. Additional analytical attacks on the nozzle flow problem are given in References 12-20 including a number of numerical solutions for particular cases.

Wegener (References 21-23) has conducted a series of interesting experiments concerning the flow of a reacting gas mixture of nitrogen dioxide and nitrogen tetroxide carried in nitrogen. This particular mixture changes color as the reaction proceeds (nitrogen dioxide is brown and nitrogen tetroxide is colorless) allowing concentration

measurements to be made by light absorption techniques. Studies of both supersonic expansions and flow through shock waves have been made, and the results agree well with theoretical predictions.

B. Statement of the Problem

This study concerns the effect of the rate of recombination on the expansion of a diatomic gas. It will be assumed that the various energy modes are not coupled and that the state of the gas can be defined by the ideal gas law if compensation is provided for the molecular weight changes as a result of the chemical reaction. Translational, rotational, and vibrational modes of energy will be included; however, all the electronic energy levels will be neglected. An algebraic form for the recombination rate will be assumed and solutions obtained for a number of different recombination rate functions.

II. GOVERNING EQUATIONS

A. One Dimensional Inviscid Conservation Equations

This investigation will consider only one dimensional flow along a streamline coordinates, r^* , in a right handed, orthogonal, curvilinear coordinate system. In the absence of sources or sinks the steady state continuity equation is

$$\frac{d}{dr} (\rho AV) = 0 \quad (2-1)$$

ρ - mass density

A - flow area

V - velocity

Neglecting electromagnetic effects and body forces, the momentum equation is

$$V \frac{dV}{dr} + \frac{1}{\rho} \frac{dp}{dr} = 0 \quad (2-2)$$

p - pressure

For adiabatic flow the energy equation is

$$\frac{dH}{dr} + V \frac{dV}{dr} = 0 \quad (2-3)$$

H - enthalpy

* Although all symbols are included in Appendix A, Nomenclature, they are defined as they are introduced in the text.

B. Auxiliary Equations

1. Thermodynamic Relationships

Only diatomic gases will be considered in this study, and it will be assumed that there is no interaction, or coupling, between the various energy modes. Therefore, the partition function, Q , for each diatomic molecule may be written as the product of the individual partition functions for the translational, vibrational, rotational, and electronic modes, or

$$Q_M = Q_{M \text{ trans}} Q_{M \text{ vib}} Q_{M \text{ rot}} Q_{M \text{ elec}}$$

Similarly, the partition function for each atom is

$$Q_A = Q_{A \text{ trans}} Q_{A \text{ elec}} Q_{A \text{ energy zero}}$$

The last term in this expression sets the reference level that is chosen for the energy zero for the atomic species at the same level as for the molecular species.

It will be further assumed that the components of the partition functions may be adequately represented by

$$Q_{\text{trans}} = \left[\frac{2 \pi m k T}{h^2} \right]^{3/2} V$$

$$Q_{\text{vib}} = \left[1 - \exp \left(-\frac{h \nu}{k T} \right) \right]^{-1}$$

$$Q_{\text{rot}} = \left[\frac{8 \pi^2 I k T}{\sigma h^2} \right]$$

$$Q_{elec} = g$$

$$Q_{energy}^{zero} = \exp \left(- \frac{E_A}{kT} \right)$$

m - particle mass

k - Boltzmann's constant

T - absolute temperature

h - Planck's constant

V - total volume

ν - characteristic frequency of molecular vibration

I - molecular moment of inertia

σ - symmetry factor

g - statistical weight (electron degeneracy) of the electronic ground state

E - dissociation energy

The partition functions for the molecules and atoms are therefore

$$Q_M = \left[\frac{2\pi(2m_A)kT}{h^2} \right]^{3/2} V \left[1 - \exp \left(- \frac{h\nu}{kT} \right) \right]^{-1} \left[\frac{8\pi^2 I kT}{\sigma h^2} \right] g_M$$

$$Q_A = \left[\frac{2\pi m_A kT}{h^2} \right]^{3/2} V g_A \exp \left(- \frac{E_A}{kT} \right)$$

The partition function for a collection of N particles is given by

$$\frac{Q^N}{N!}$$

The factorial is necessary because in the derivation of the translational partition function it was assumed that the individual particles

were distinguishable and they are not. Now, all of the thermodynamic functions may be defined in terms of the partition function and its derivatives. (It is convenient to choose N equal to Avagadro's number and use a molar basis for these calculations.)

The Helmholtz free energy may be written as

$$A = - kT \ln \frac{Q^N}{N!}$$

The pressure and the entropy are related to the partition function by

$$p = - \left. \frac{\partial A}{\partial V} \right|_T$$

$$S = - \left. \frac{\partial A}{\partial T} \right|_V$$

The enthalpy may be written as

$$H = A + TS + pV$$

and the Gibbs free energy as

$$F = A + pV$$

Although some of the restrictions inherent in the assumptions relating to the partition functions will become obvious or will be examined in greater detail in the following sections, more extensive discussions of these items may be found in References 24 and 25.

2. Equation of State

Using Sterling's approximation for the factorial of large numbers

$$\ln N! = N \ln N - N$$

the Helmholtz free energy may be written

$$A = -RT \left[\ln \frac{Q}{N} + 1 \right]$$

and the partial pressure exerted by the molecular or atomic species is

$$p = \frac{RT}{V}$$

Rewriting in terms of mass density and adding the partial pressures of the two mixture components, the total pressure becomes

$$p = \rho \frac{R}{2M_A} T (1 + \alpha) \quad (2-4)$$

in which α is defined as the mass fraction of the dissociated species

$$\alpha = \frac{p_A}{p} \quad (2-5)$$

Inspection of Equation (2-4) shows that it is the classical ideal gas equation of state with the molecular weight corrected for the mass fraction of the dissociated species.

3. Enthalpy

Combining terms, the enthalpy of either species may be written

$$H = RT^2 \left[\frac{d}{dT} \ln \frac{Q}{N} \right]_V + RT$$

The enthalpies of the atomic and molecular species are therefore

$$H_M = \frac{5}{2} RT + R \frac{h\nu}{k} \left[\exp \left(\frac{h\nu}{kT} \right) - 1 \right]^{-1} + RT$$

$$H_A = \frac{3}{2} RT + NE_A + RT$$

Rewriting in terms of mass units and adding the contributions of both components, the enthalpy of the mixture is

$$H = \frac{R}{4M_A} (7 + 3\alpha) T + \frac{NE_A}{M_A} \alpha + \frac{R}{2M_A} \frac{h\nu}{k} (1 - \alpha) \left[\exp \left(\frac{h\nu}{kT} \right) - 1 \right]^{-1} \quad (2-6)$$

The degree of approximation in the calculation of the enthalpy may be seen by examining Figures 2-1 and 2-2. Using the data of Heims (Reference 26), the contributions of the various energy modes are shown for molecular and atomic oxygen. Although the electronic partition function has been assumed equal to its ground statistical weight and thus the electronic energy has been neglected, this results in only a negligible amount of error. The electronic contribution to the enthalpy of molecular oxygen is more significant, especially at the higher temperatures; however, dissociation decreases the concentration of the molecular species at higher temperatures and consequently the electronic energy of the molecules may also be neglected without significant error. Almost without exception, other investigators have used the model of a dissociating gas proposed by Lighthill (Reference 27).

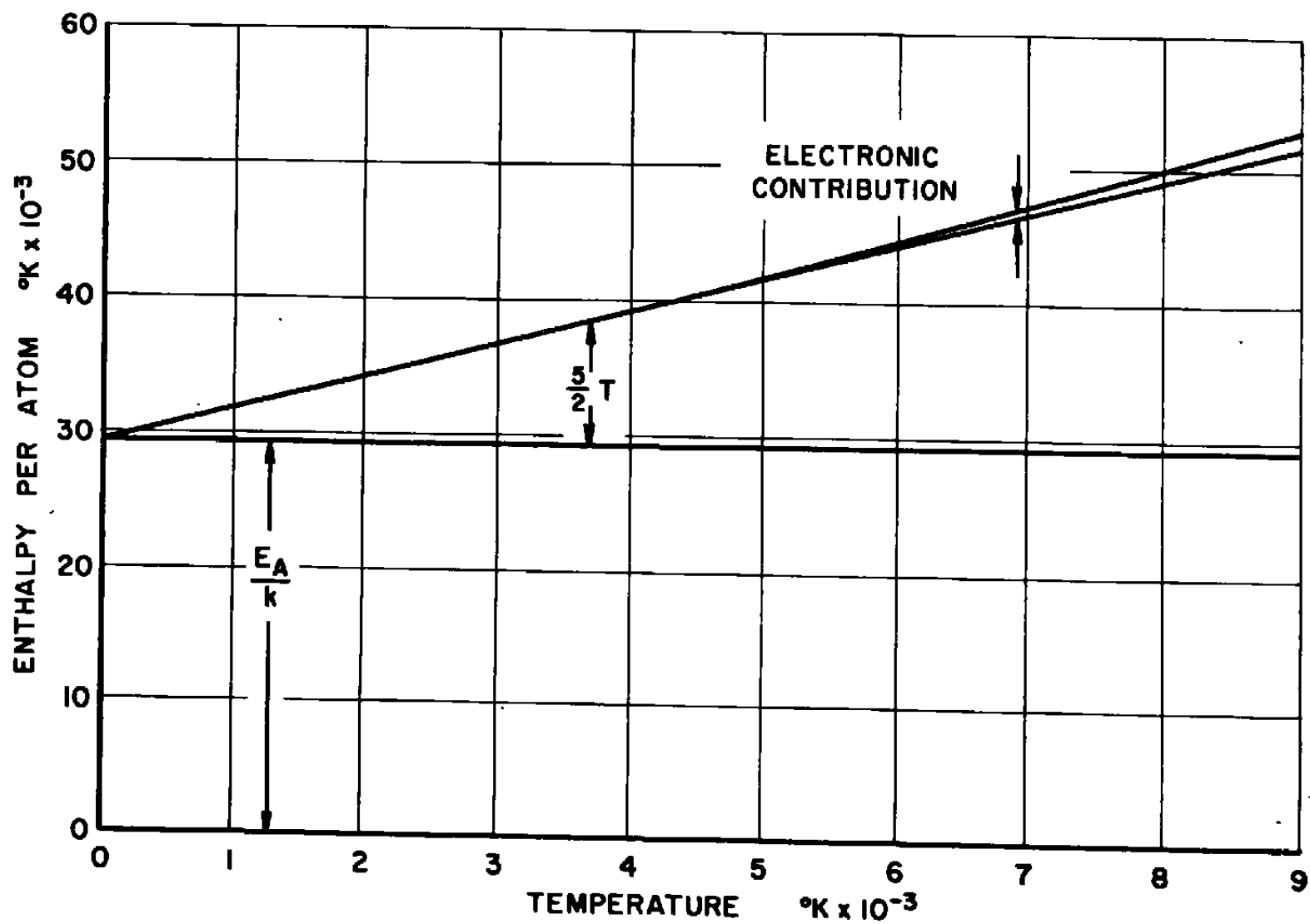


FIGURE 2-1 ENTHALPY OF ATOMIC OXYGEN

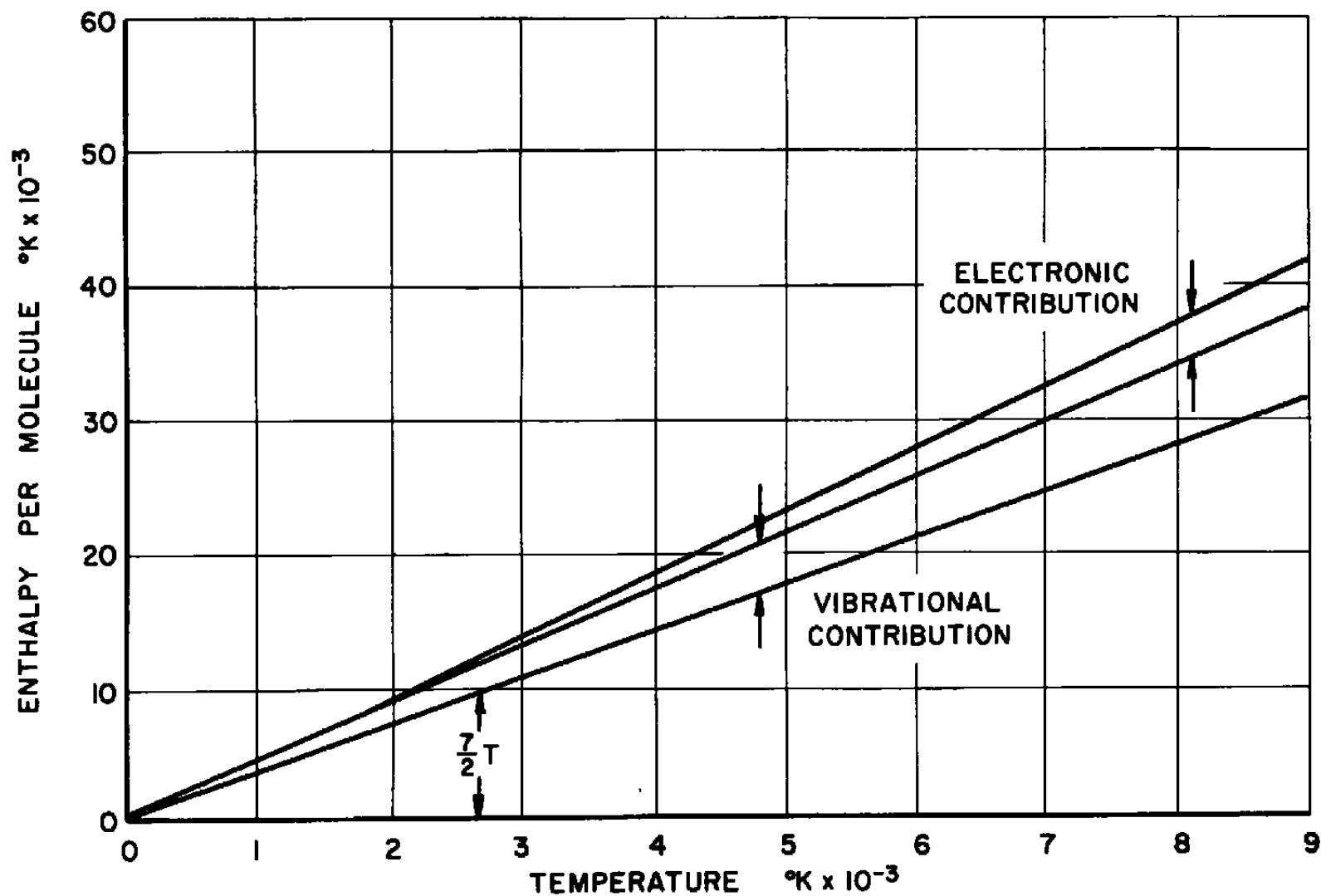


FIGURE 2-2 ENTHALPY OF MOLECULAR OXYGEN

Equation (2-6) corrects Lighthill's "ideal dissociating gas" through the fact that it allows a variation in the vibrational energy of the molecular species and the translational energy of the dissociated species.

4. Equilibrium Constant

The equilibrium constant based on partial pressures, K_p , may be written in terms of the Gibbs free energy as

$$\ln K_p = - \frac{\Delta F^0}{RT}$$

(The superscript 0 indicates that the free energies are evaluated at the standard state of one atmosphere.) In terms of the partition functions, the equilibrium constant for the dissociation of a diatomic gas may be written

$$K_p = \left[\frac{Q_A^0}{N} \right]^2 / \left[\frac{Q_M^0}{N} \right]$$

or, combining the ideal gas law and the partition functions

$$K_p = \frac{1}{8\pi^{1/2} h} \left[\frac{k}{N} \right]^{3/2} \frac{M_A^{3/2} \sigma}{I} \frac{q_A^2}{q_M} T^{3/2} \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right] \exp\left(-\frac{2E_A}{kT}\right)$$

This equation represents the equilibrium constant only if the electronic contributions to the energy are negligible. However, due to the high temperatures required for significant dissociation, this assumption is questionable. Hanson (Reference 28) has calculated the equilibrium constant for oxygen including two electronic levels past

the ground state for the molecule and four electronic levels past the ground state for the atom. Hanson's results are compared to the values predicted by the above equation in Figure 2-3. The comparison is not too good. Further consideration and an analysis of the effect of higher electronic states reveals that the electronic states for the atom are much more significant than the electronic states for the molecule. This fortunate characteristic allows a much better approximation to the equilibrium constant to be made by neglecting the vibrational term for the molecules to offset the electronic terms, see Figure 2-3. Therefore the equilibrium constant may be considered to be

$$K_p = \frac{1}{8 \pi^{1/2} h} \left[\frac{k}{N} \right]^{3/2} \frac{M_A \sigma}{I} \frac{q_A^2}{q_M} T^{3/2} \exp \left(- \frac{2E_A}{kT} \right) \quad (2-7)$$

In this study, this representation of the equilibrium constant has been corrected slightly by evaluating the coefficient to give the exact result at a temperature near the maximum temperature considered. Light-hill's "ideal dissociating gas" uses a similar approximation for the equilibrium constant. Equation (2-7) incorporates additional rigor, since it includes an additional square root of temperature correction.

5. Recombination Rate

The recombination of atoms to form diatomic molecules is generally considered a termolecular reaction in which three individual particles participate in a single kinetic process, the third particle being necessary to remove the energy of recombination. Numerous theories have been advanced to predict the value of the recombination rate for this type of reaction, and References 8, 29, and 30 contain discussions of some of

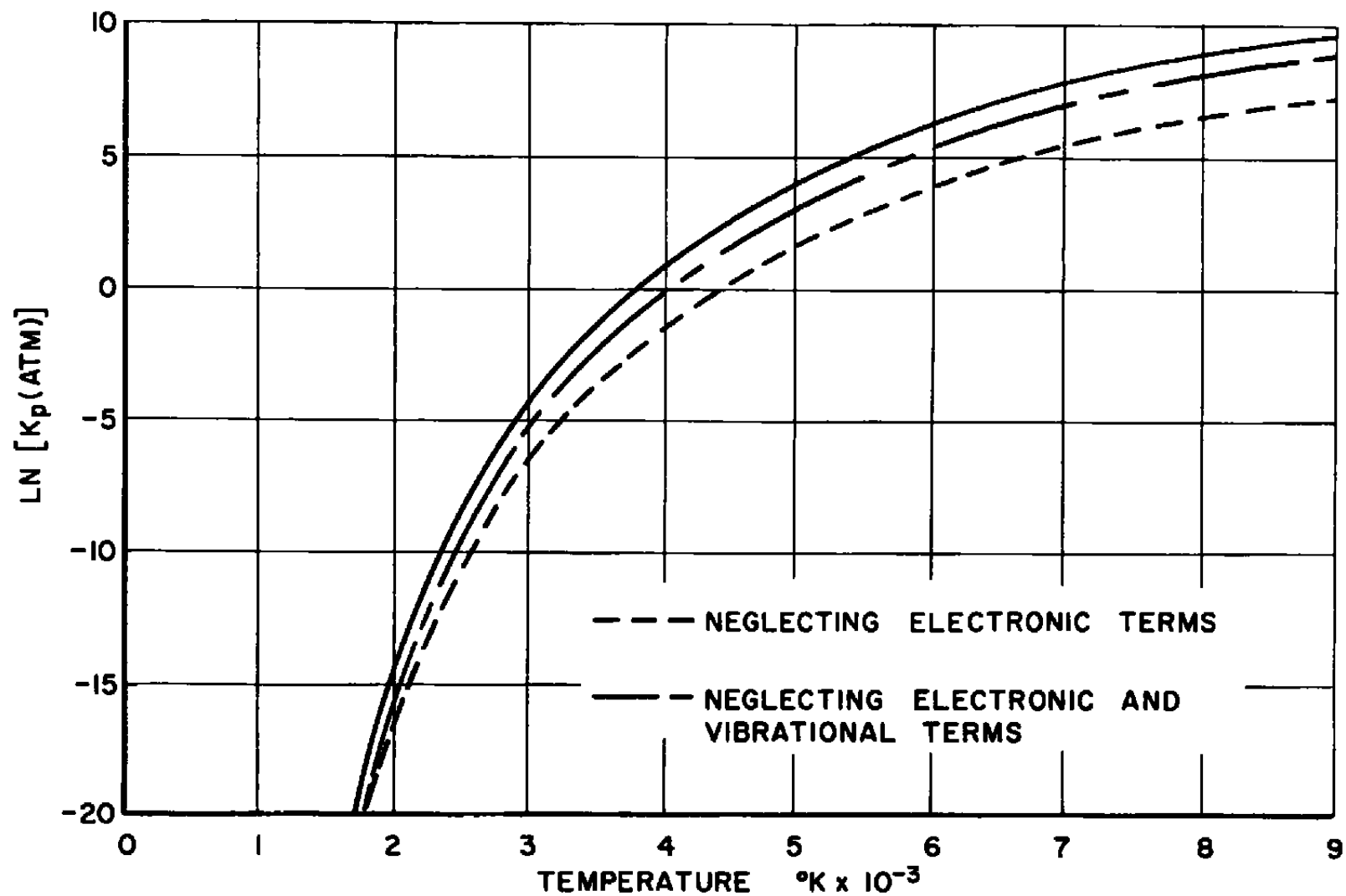


FIGURE 2-3 EQUILIBRIUM CONSTANT FOR $\text{O}_2 \rightleftharpoons 2\text{O}$

these theories. Unfortunately, the various approaches do not agree, particularly regarding the temperature dependence. In general it may be concluded that the activation energy required for the recombination process is negligible and the recombination rate has an algebraic temperature dependence.

$$k_R \sim T^n \quad (2-8)$$

The lack of agreement from this point on is evident upon examination of Table 2-1 (abstracted from Reference 29). This table lists the values of the recombination rate for oxygen currently set forth in the literature. Experimental data for this and other high temperature reactions is sparse and questionable, since in general the dissociation rate is measured and the equilibrium constant then used to calculate the recombination rate. The large activation energy required for dissociation is included in an exponential temperature dependence which effectively masks the exact value of n in Equation (2-8). This study is of the effect of various recombination rates and the form of Equation (2-8) is satisfactory.

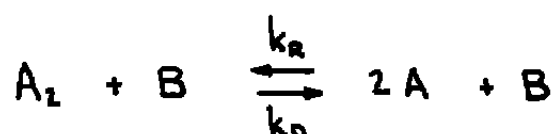
C. Reaction Equation

Dissociation of a diatomic molecule may be considered to be the result of a collision between a molecule and another particle if sufficient energy is available to break the molecular bond. Similarly, recombination may be considered to be the result of a collision between two atoms in the presence of a third particle. The opposing reactions of dissociation and recombination may be represented as

Recombination Rate
 $\text{cm}^6 \text{ gm-mole}^{-2} \text{ sec}^{-1}$

| | | |
|-----------------------|-----------------|------|
| 2.6×10^{17} | $\frac{T}{300}$ | -2 |
| 4.05×10^{17} | $\frac{T}{300}$ | -1.5 |
| 4.53×10^{17} | $\frac{T}{300}$ | -0.5 |
| 3×10^{15} | $\frac{T}{300}$ | 0.5 |
| 1.2×10^{16} | $\frac{T}{300}$ | 2.5 |

Table 2-1 Recombination Rate for Oxygen



k_D - dissociation rate

k_R - recombination rate

The dissociation rate is defined as

$$\left. \frac{\rho}{M_A} \frac{d\alpha}{dt} \right|_D = 2k_D \left[\frac{\rho(1-\alpha)}{2M_A} \right] \left[\frac{\rho(1+\alpha)}{2M_A} \right]$$

(The rate of production of dissociated species is proportional to the concentration of the diatomic species times the total concentration of the mixture.) The recombination rate is defined as

$$\left. \frac{\rho}{M_A} \frac{d\alpha}{dt} \right|_R = -2k_R \left[\frac{\rho\alpha}{M_A} \right]^2 \left[\frac{\rho(1+\alpha)}{2M_A} \right]$$

The net change of the atomic species is therefore the sum of these two expressions. Expanding the Eulerian derivative and restricting it to steady flow, this sum becomes

$$\frac{d\alpha}{dr} = \frac{k_R}{V} \frac{\rho(1+\alpha)}{M_A} \left[\frac{k_D}{k_R} \frac{(1-\alpha)}{2} - \frac{\rho\alpha^2}{M_A} \right]$$

A particular case for which there is no net rate of production of either chemical species is a chemical equilibrium state. For equilibrium the above equation reduces to

$$\frac{k_D}{k_R} = \frac{2}{M_A} \frac{\rho\alpha^2}{(1-\alpha)}$$

or, in terms of partial pressures

$$\frac{k_D}{k_R} = \frac{1}{RT} \frac{p_A^2}{p_M}$$

Inspection shows that this ratio of partial pressures is equivalent to the equilibrium constant for the reaction being considered. Therefore

$$\frac{k_D}{k_R} = \frac{K_p}{RT}$$

Although the above equation has been derived for the particular case of a system in equilibrium (and thus no change in composition), it will be used for this problem since it is generally agreed that k_D , k_R , and K_p are all only functions of temperature and not composition and the relationship will hold for all cases in which a mixture temperature can be defined. Feldman (Reference 31) states that this ratio may be used in non equilibrium cases when the individual particles have an equilibrium statistical distribution of their energy levels. This therefore reduces to the assumption that the relaxation times for the various energy modes is very short compared to the relaxation time required to attain chemical equilibrium.

The species continuity equation, or reaction equation, for the nozzle flow problem may now be written as

$$\frac{d\alpha}{dr} = \frac{k_R}{V} \frac{\rho(1+\alpha)}{M_A} \left[\frac{K_p}{RT} \frac{(1-\alpha)}{2} - \frac{\rho\alpha^2}{M_A} \right] \quad (2-9)$$

D. Summary of Non Dimensionalised Equations

A set of equations describing the flow of a reacting diatomic gas have been developed. To facilitate subsequent computations, the

area, distance, velocity, temperature, density, and pressure can be non dimensionalised with respect to some reference conditions, indicated by the subscript 0. The resulting equations are

Continuity Equation

$$d(\rho A V) = 0 \quad (2-10)$$

Momentum Equation

$$dp = -\beta \rho V dV \quad (2-11)$$

$$\beta = \frac{2MA}{RT_0} \eta V_0^2 \quad (2-12)$$

$$\eta = \frac{1}{1+\alpha_0} \quad (2-13)$$

Energy Equation

$$V dV + \frac{\eta}{\beta} d \left[\frac{1}{2} (7+3\alpha) T + D\alpha + \Theta (1-\alpha) J \right] = 0 \quad (2-14)$$

$$D = \frac{2NE_A}{RT_0} \quad (2-15)$$

$$\Theta = \frac{h\nu}{kT_0} \quad (2-16)$$

$$J(T) = \left[\exp\left(\frac{\Theta}{T}\right) - 1 \right]^{-1} \quad (2-17)$$

Equation of State

$$p = \eta p T (1 + \alpha) \quad (2-18)$$

Reaction Equation

$$\frac{d\alpha}{dr} = \frac{\beta^{1/2}}{\eta^{3/2}} F \frac{p}{V} \left[\frac{1}{\eta} G(1-\alpha) - p\alpha^2 \right] \quad (2-19)$$

$$F(T) = \sqrt{\frac{2MA}{RT_0}} \quad \frac{4p_0^2 r_0}{R^2 T_0^2} \quad \frac{k_R}{T} \quad (2-20)$$

$$G(T) = \frac{1}{4p_0} \quad \frac{K_p}{T} \quad (2-21)$$

III. SOLUTIONS AND DISCUSSION OF RESULTS

A. General Considerations

The reference conditions with which the dimensionless variables are formed are most conveniently chosen to be those at the nozzle throat. Examination of the continuity equation shows that this corresponds to the point at which

$$\left. \frac{d\rho}{dV} \right|_0 = -1$$

For a variety of particular cases this equation provides an explicit definition for the value of β (which is a function of the critical velocity at the nozzle throat). However, in general this condition will be related to the nozzle geometry through the reaction equation and the recombination rate function. Physically, β can be considered to be an effective ratio of specific heats, since it performs a function similar to that ratio in classical gas dynamics.

Analysis of the equations listed in the preceding section shows that both the continuity equation and the energy equation may be integrated directly with the results

$$\rho A V = 1 \quad (3-1)$$

$$V^2 = 1 + \frac{\eta}{\beta} \left[(7+3\alpha_0) - (7+3\alpha) T + 2D (\alpha_0 - \alpha) + 2\Theta (1-\alpha_0) I_0 - 2\Theta (1-\alpha) I \right] \quad (3-2)$$

Since the equation of state is an algebraic equation and can be solved explicitly, the problem that remains is the integration of the momentum equation and the reaction equation. A careful study of the reaction equation indicates that it would be extremely difficult to integrate analytically, even for very simple cases. However, once the remainder of the problem has been solved, the reaction equation may be evaluated either numerically or graphically, to obtain the nozzle contour. It can be partially integrated to

$$(r-1) = \int_{r=1}^{r=r} \frac{\eta^{3/2} V d\alpha}{\beta^{1/2} F p \left[\frac{1}{\eta} G (1-\alpha) - p\alpha^2 \right]} \quad (3-3)$$

Analytical solutions to the momentum equation may be obtained for a few cases, but in general numerical techniques must be employed.

B. Analytical Solutions

1. Frozen Flow

If the recombination rate is slow enough so that the composition of the flow does not change appreciably during the nozzle expansion, the flow is said to be frozen. This may be considered to be the case for which Damkohler's first coefficient is

$$Dam \gg 1$$

Since it is defined as a characteristic time for reaction divided by

the residence time in the nozzle. In this case the conditions at the nozzle throat must be such that

$$(\beta-1) = \frac{2(1+\alpha_0)}{(5+\alpha_0) + 2(1-\alpha_0)\Theta^2 J_0 (J_0+1)} \quad (3-4)$$

Figure 3-1 gives this result graphically for the initial conditions described in Appendix C.

The general equation for flow velocity, Equation (3-2) may be specialized to the case of frozen flow.

$$V^2 = 1 + \frac{\eta}{\beta} \left[(7+3\alpha_0)(1-\tau) + 2\Theta(1-\alpha_0)(J_0-J) \right] \quad (3-5)$$

The momentum equation can be integrated for this case by combining it with the velocity and the equation of state. The result is

$$p = \tau^{\frac{\eta}{2}(7+3\alpha_0)} \left[\frac{J_0+1}{J+1} \right]^{\eta(1-\alpha_0)} \exp \left[\eta \Theta (1-\alpha_0) J_0 \left(1 - \frac{1}{\tau} \frac{J}{J_0} \right) \right] \quad (3-6)$$

2. Isothermal Flow

An isothermal flow can be maintained throughout the nozzle expansion if sufficient energy is released by the recombination of atoms. In this case the conditions at the nozzle throat must be such that

$$(\beta-1) = \frac{1}{\left(\frac{1}{2} + D \right) + \Theta J_0} \quad (3-7)$$

This condition is graphically represented on Figure 3-1.

Specializing the velocity to the case of an isothermal flow, the result is

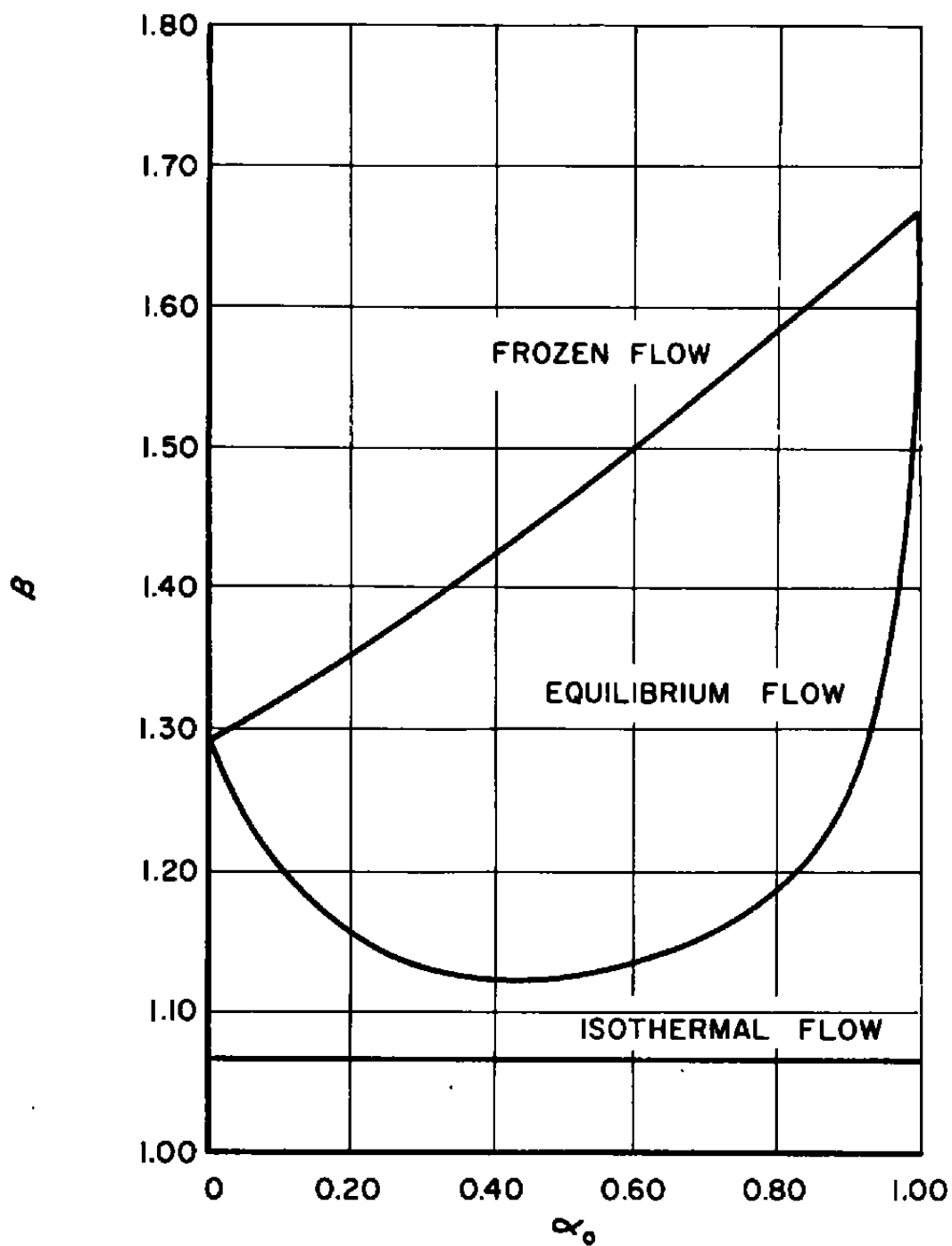


FIGURE 3-1 THROAT CONDITIONS

$$V^2 = \frac{(\beta+1)}{(\beta-1)} - \frac{2\eta}{(\beta-1)} (1+\alpha) \quad (3-8)$$

Again the momentum equation may be integrated if this equation is combined with the equation of state and the pressure may be expressed as

$$p = \left[\eta (1+\alpha) \right]^{\frac{\beta}{\beta-1}} \quad (3-9)$$

3. Equilibrium Flow

If the reaction time is very short compared to the residence time, or

$$Da_m \ll 1$$

the flow is said to be an equilibrium flow and the composition is a unique function of the equilibrium constant and the pressure. For equilibrium flow the throat conditions must be such that

$$\begin{aligned} (\beta-1) = & \left\{ 2(2-\alpha_o)(1+\alpha_o)^2 - \alpha_o(1-\alpha_o) \left[(7+3\alpha_o) + 2\Theta^2(1-\alpha_o) \cdot \right. \right. \\ & \left. J_o(J_o+1) \right] + 2\alpha_o(1+\alpha_o)(1-\alpha_o) \left[2\left(\frac{1}{2}+D\right) + (1-\Theta J_o) \right] \right\} \div \\ & \left\{ (2-\alpha_o)(1+\alpha_o) \left[(5+\alpha_o) + 2\Theta^2(1-\alpha_o) J_o(J_o+1) \right] \right. \\ & \left. + 2\alpha_o(1-\alpha_o)\left(\frac{1}{2}+D\right) \left[\left(\frac{1}{2}+D\right) + (1-\Theta J_o) - 1 \right] \right\} \quad (3-10) \end{aligned}$$

The restriction of equilibrium flow does not produce a significant simplification for the momentum equation, and it still cannot be integrated. Numerous charts and tables for equilibrium properties have been published, i.e., Reference 3, to facilitate numerical calculations.

4. Isobaric-Isovel Flow

Although perhaps not too interesting in a physical sense, an analytical solution may be obtained for the case of constant pressure flow. Application of the criterion for the nozzle throat yields

$$3 + \frac{(7 + 3\alpha_0)}{(1 + \alpha_0)} + 2D - 2\Theta J_0 \left[1 - \Theta J_0 \frac{(1 - \alpha_0)}{(1 + \alpha_0)} \exp \Theta \right] = 0 \quad (3-11)$$

Inspection of this equation shows that the condition for a throat requires an exothermic dissociation reaction. If such a gas were used, a unique throat temperature would be required as specified by the above equation. A convergent-divergent nozzle is impossible for the gases considered in Appendix C; however, purely convergent or divergent sections may produce constant pressure flows.

Through the momentum equation it can be seen that a constant pressure flow must correspond to a constant velocity flow and the momentum equation reduces to a trivial identity.

5. Constant Density Flow

For constant density flow the conditions at the nozzle must be such that either

$$F_o = 0 \quad (3-12)$$

or

$$G_o = \frac{\kappa_o^2}{(1 - \kappa_o^2)} \quad (3-13)$$

The first restriction corresponds to the classical case of an incompressible flow with no reaction. The alternate restriction requires that the throat composition be an equilibrium composition. In neither case is a unique throat velocity defined.

6. Discussion

Some rather interesting results can be deduced from a careful study of Figure 3-1. β represents an effective ratio of specific heats in defining the critical velocity of a reacting gas flow at the throat of a nozzle. For the classical case it varies from 7/5 for a diatomic gas to 5/3 for a monatomic gas. However, this familiar range is inexact, since the vibrational energy has not been included. Figure 3-2 shows that the inclusion of the vibrational term lowers the effective specific heat ratio by approximately 8 per cent. Since this is the ratio of two temperature dependent functions and varies less than either of them alone, it could be anticipated that there would be a considerable correction in the calculation of the other flow parameters if the vibrational energy is neglected. The redeeming feature is that a very high pressure would be required to exactly approach this extreme case at the fixed temperature of 4050 K for which the curves are drawn.

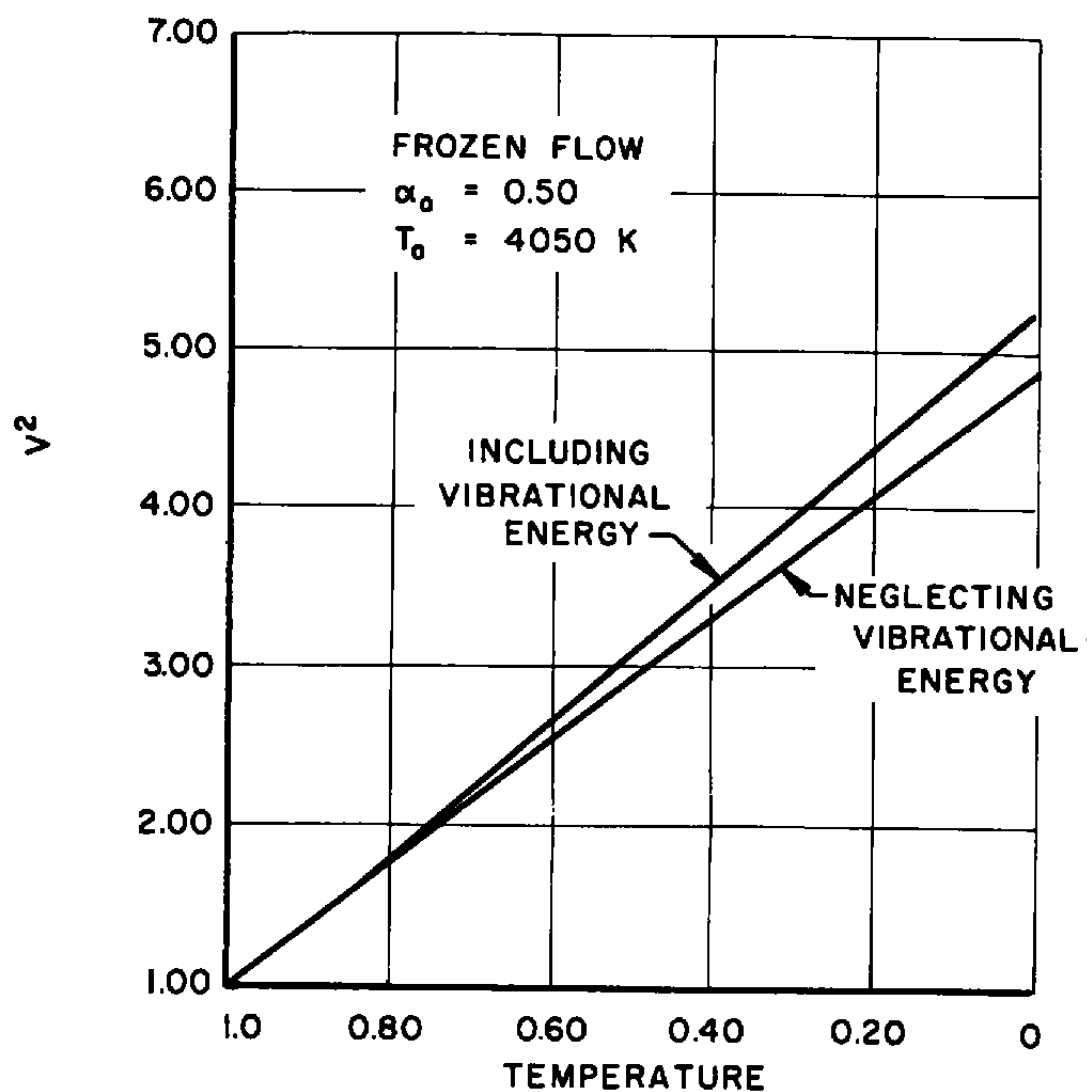


FIGURE 3-2

EFFECT OF VIBRATIONAL ENERGY
ON VELOCITY

However, the inclusion of the vibrational energy continues to have an effect, of decreasing magnitude, as the composition changes to the other extreme of a pure monatomic gas (corresponding to a very low pressure). Therefore, except for almost completely dissociated flows, the vibrational terms should be considered. Figure 3-2 shows that this error can exceed 3 per cent in the velocity for $\alpha_0 = 0.50$. Of course the error will be greater for smaller values of α .

The β for equilibrium flow matches that for frozen flow at the end points (the limiting cases of the zero and infinite pressure) and drops sharply in the intermediate range, approaching the case of isothermal flow. This follows from the fact that in this region the composition is particularly sensitive to pressure. The value of β for the isothermal flow of a reacting gas is independent of composition and close to unity. In the limiting case of an infinite dissociation energy, it is exactly unity and the flow behaves similarly to the classical isothermal flow, studied by Romer and Cambl and reported in Reference 32, since no change in composition would be required to maintain the temperature. The throat velocity then corresponds to Newton's isothermal speed of sound.

When considering the flow of a reacting gas, it is well to remember that the composition must be approaching equilibrium. The deviation from equilibrium might increase throughout the expansion process, but this must result from the equilibrium point changing more rapidly than the flow can follow. Considering this, isothermal flow can exist only if $\alpha > \alpha_e$, since this will necessarily result in recombination,

the rate being controlled by the recombination rate function, F .

C. Computer Solutions

1. Nozzle Contour

The inclusion of the species continuity equation with the conventional gas dynamic conservation equations has added two additional variables, the composition and the nozzle geometry. Therefore an additional equation describing the nozzle contour is required to obtain solutions. The primary purpose of this study is to examine the effect of the recombination rate and thus the choice of nozzle contour is arbitrary. The most convenient contour

$$r = A \quad (3-14)$$

has been chosen and is shown in Figure 3-3. This particular shape has several noteworthy characteristics. Primarily, it simplifies the equations and decreases the complexities of the computer program. In addition it is fluid mechanically feasible since the maximum value of the half angle in the expansion is approximately 15 degrees. In addition, it forces the reaction equation to predict a zero derivative for the composition at the throat, greatly simplifying the setting of the initial conditions (see Appendix C). The major disadvantage of this nozzle is that it does not actually have a throat, or minimum point, but since the temperature must decrease as a result of the computer program, this difficulty is minor.

2. Computer Equations

Considerable care must be given to the formulation of the equations

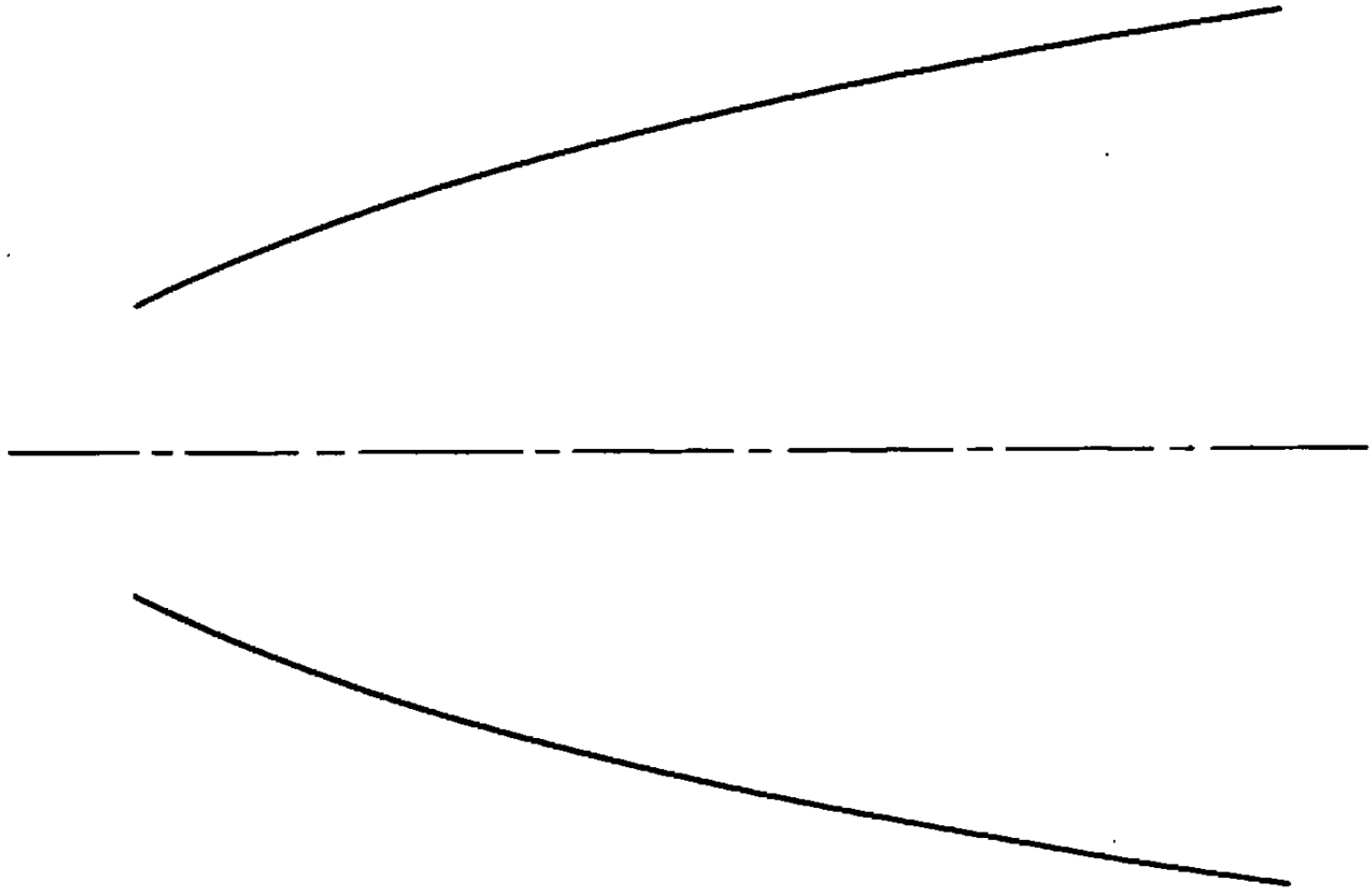


FIGURE 3-3

NOZZLE CONTOUR

and scaling of the variables before they can be programmed for solution on an analog computer (details are presented in Appendix D). It will suffice to note that scaling was

$$T = 1 = 100v$$

$$p = 1 = 100v$$

$$K = 1 = 100v$$

$$\frac{p}{T} = 1 = 100v$$

$$\frac{1}{A} = 1 = 100v$$

and the machine time was slowed down by a factor of 10. After considerable manipulation, the computer equations can be written as (N is the reciprocal of the area)

$$-\frac{dT}{dt} = \frac{1}{1000} T^2 \quad (3-15)$$

$$-\frac{dJ}{dt} = \frac{1}{10} \Theta J(J+1) \quad (3-16)$$

$$\begin{aligned} -\frac{dv^2}{dt} = & -\frac{\eta}{\beta} \left[\frac{7}{10,000} T^2 + \frac{3}{1,000,000} K T^2 - 20 \Theta \frac{dJ}{dt} \right. \\ & + \frac{1}{5} \Theta K \frac{dJ}{dt} + \frac{1}{5} \Theta J \frac{dK}{dt} - \frac{3}{1000} T \frac{dK}{dt} \\ & \left. - \frac{1}{5} D \frac{dK}{dt} \right] \quad (3-17) \end{aligned}$$

$$-\frac{d}{dt}\left(\frac{p}{T}\right) = -\frac{1}{100} \frac{p}{T} \left[\frac{1}{10} T - 50,000 \frac{\beta}{\eta} \frac{1}{T(100+\alpha)} \frac{dV^2}{dt} \right] \quad (3-18)$$

$$-\frac{dN}{dt} = -\frac{1}{100} N \left[\frac{1}{10} T - 50,000 \frac{\beta}{\eta} \frac{1}{T(100+\alpha)} \frac{dV^2}{dt} + 50 \frac{1}{V^2} \frac{dV^2}{dt} - 100 \frac{1}{(100+\alpha)} \frac{d\alpha}{dt} \right] \quad (3-19)$$

$$-\frac{dG}{dt} = \frac{1}{2000} GT + \frac{1}{10} DG \quad (3-20)$$

$$\frac{d\alpha}{dt} = \frac{1}{5} \frac{\eta^{3/2}}{\beta^{1/2}} \frac{FT}{V^2} \frac{1}{N} \frac{dN}{dt} \left[\frac{1}{10,000} \alpha^2 (50G + \frac{1}{2} \frac{p}{T}) - 50G \right] \quad (3-21)$$

$$\frac{d}{dt} \left[\frac{FT}{V^2} \right] = \frac{FT}{V^2} \left[-\frac{1}{1000} nT - \frac{1}{V^2} \frac{dV^2}{dt} \right] \quad (3-22)$$

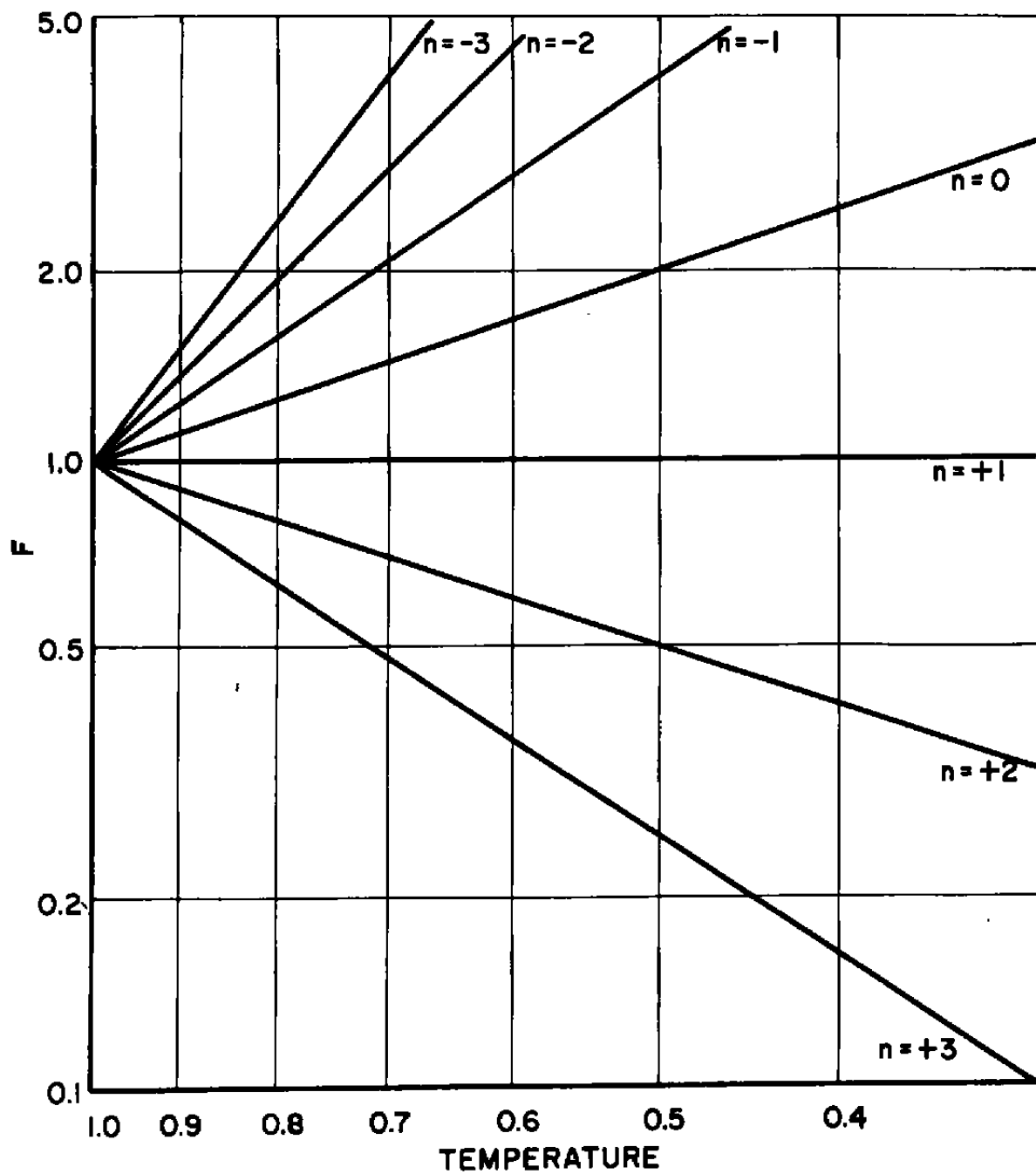
A complete discussion of boundary conditions is given in Appendix C. Three main cases were studied depending upon the initial composition, equilibrium, above equilibrium, and below equilibrium. For each of these main cases, seven subcases of different temperature dependence of

the recombination function are examined. The spectrum of recombination functions are shown in Figure 3-4.

3. Results and Discussion

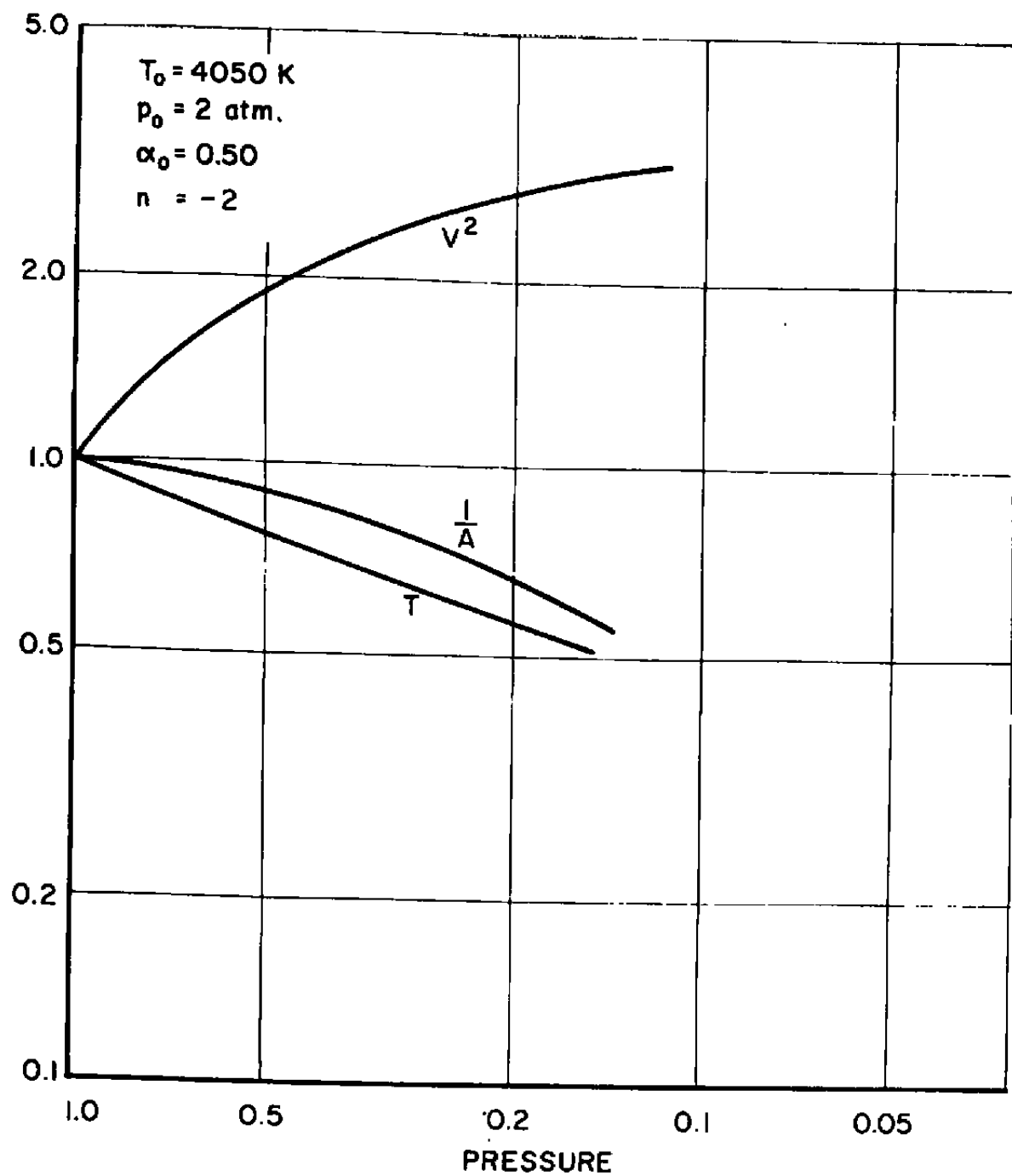
Typical solutions from the analog computer are shown in Figures 3-5, 3-6, and 3-7. The flow variables behave as expected and the pressure-temperature curve is slightly bowed as a result of the inclusion of the vibrational energy as well as the recombination reaction. The value of V^2 (essentially the M^2 of classical gas dynamics) rises rapidly and then approaches an asymptotic value (for frozen flow this must lie between 4.0 (monatomic gas) and 6.25 (diatomic gas)).

The chemical effects in the flow stream are more interesting than the fluid mechanical variables. Figures 3-8, 3-9, and 3-10 show the change in chemical composition as a function of temperature. Previous investigators, i.e., References 19 or 20, have indicated that at the low pressures studied here the amount of chemical reaction occurring downstream of the nozzle throat should be negligible. Thus the solution may be adequately represented by the frozen flow solution. This conclusion is substantiated from this study for those cases with the recombination rate an increasing function of temperature ($n > 0$). For these cases the recombination rate function becomes small quickly, and thus the chemical reaction dies out rapidly, before a significant change in composition can occur. The effect of the dissociation energy is greatly diluted if there is only a small composition change over a large temperature drop. Since the molecular weight correction is a $(1 + K)$ term, small changes in composition will have negligible effects on the

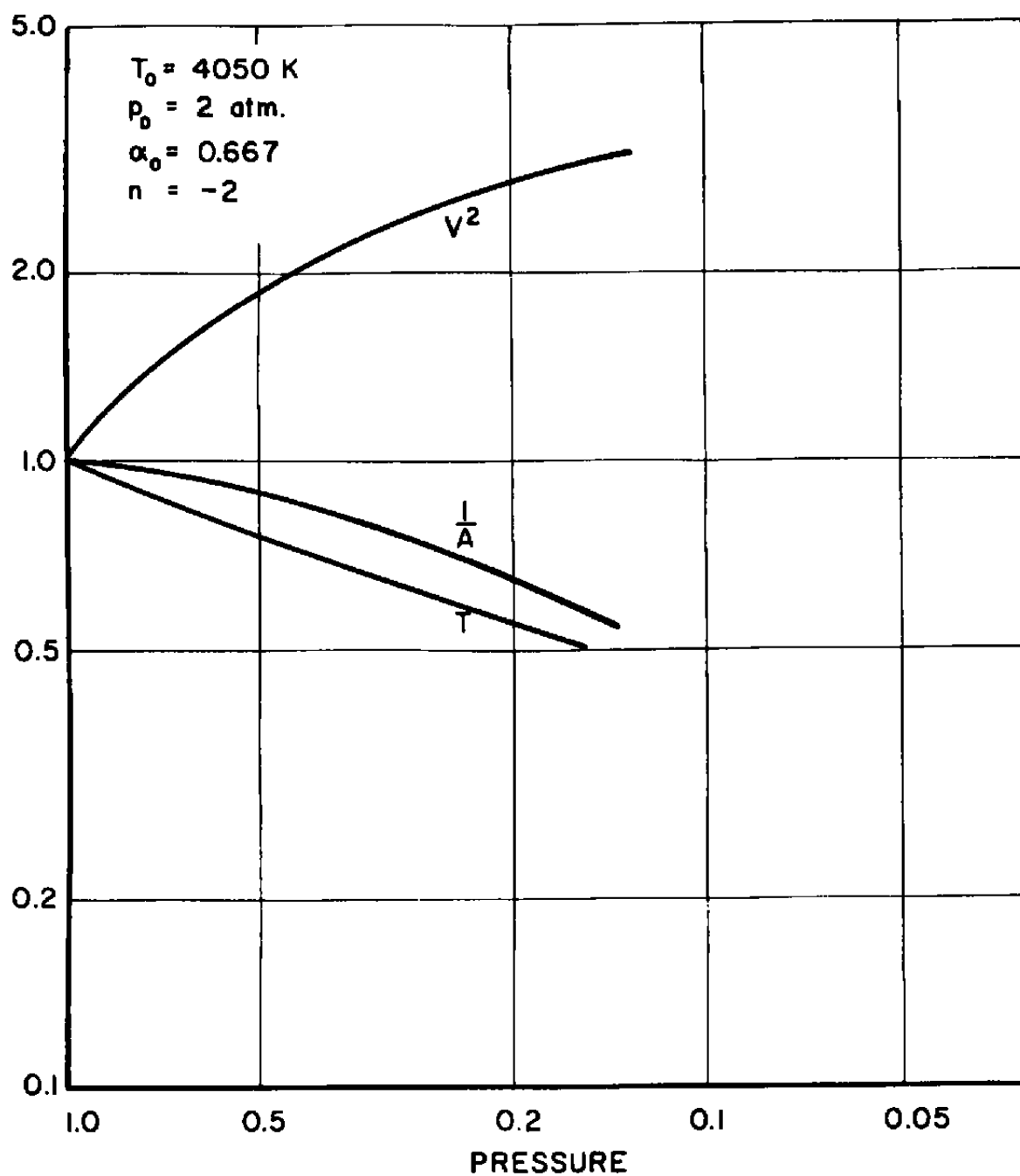


RECOMBINATION RATE FUNCTION

FIGURE 3-4

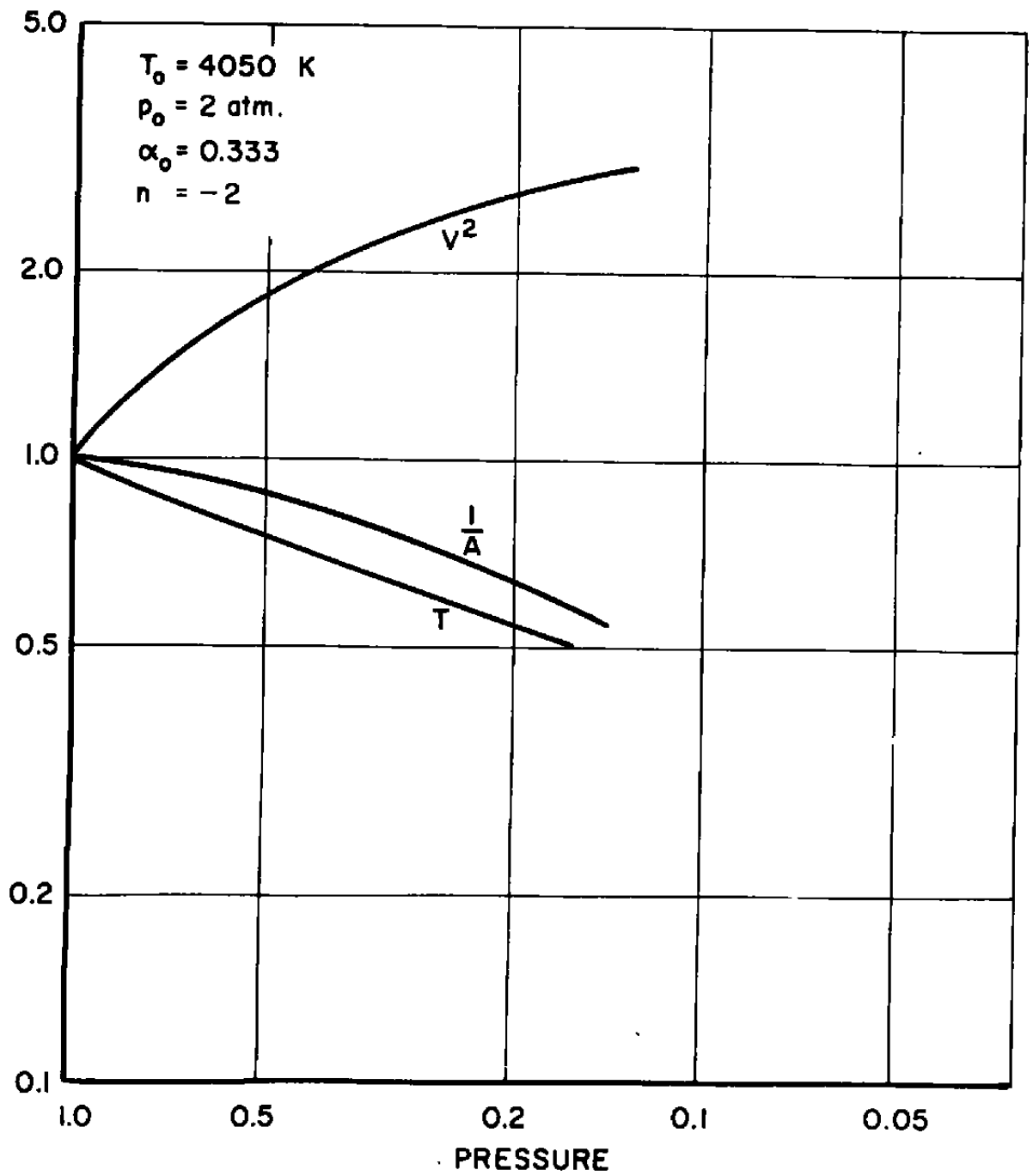


NOZZLE FLOW PARAMETERS, CASE ID
FIGURE 3-5



NOZZLE FLOW PARAMETERS, CASE IID

FIGURE 3-6



NOZZLE FLOW PARAMETERS, CASE III D
FIGURE 3-7

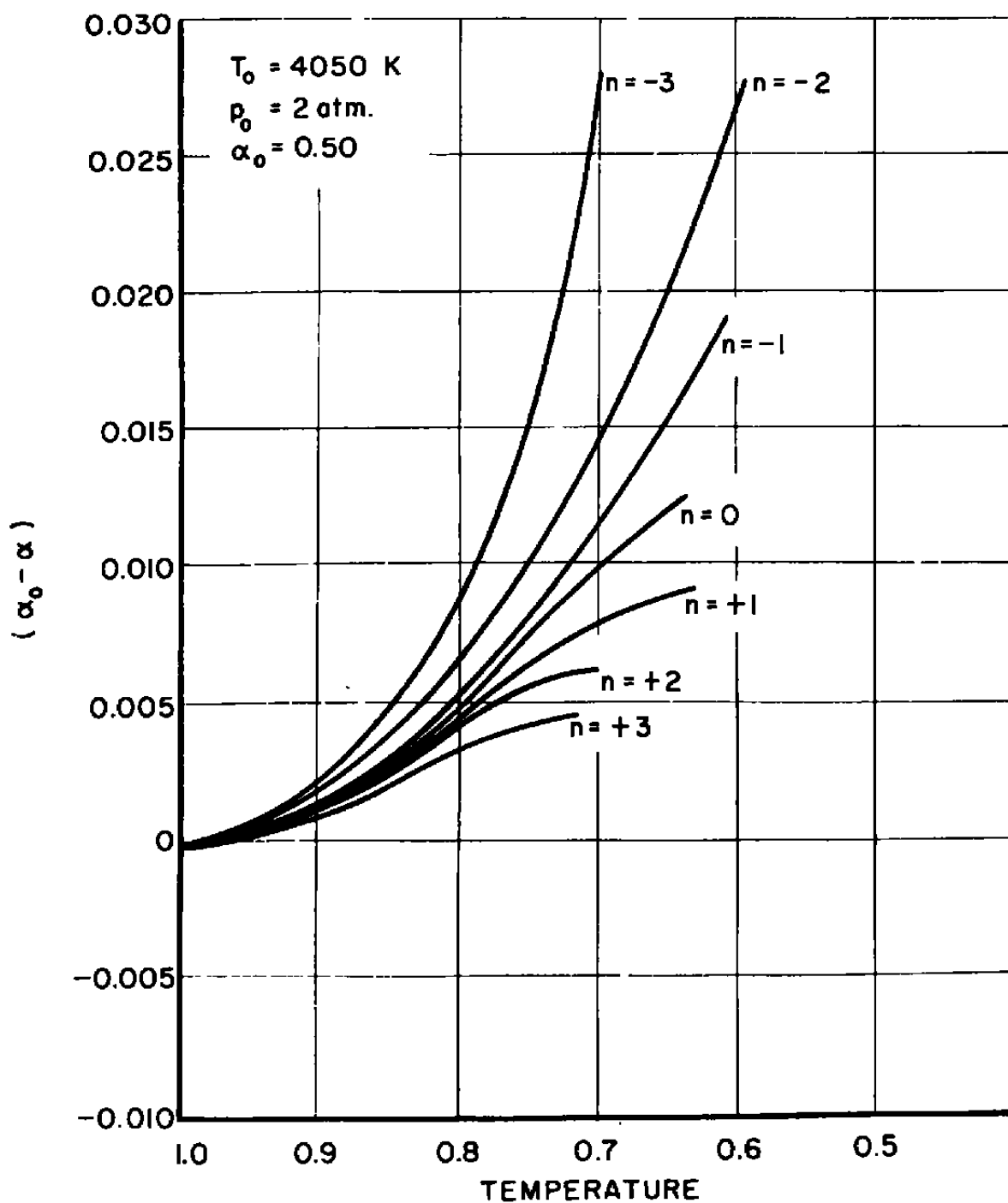


FIGURE 3-8 FLOW COMPOSITION, CASE I

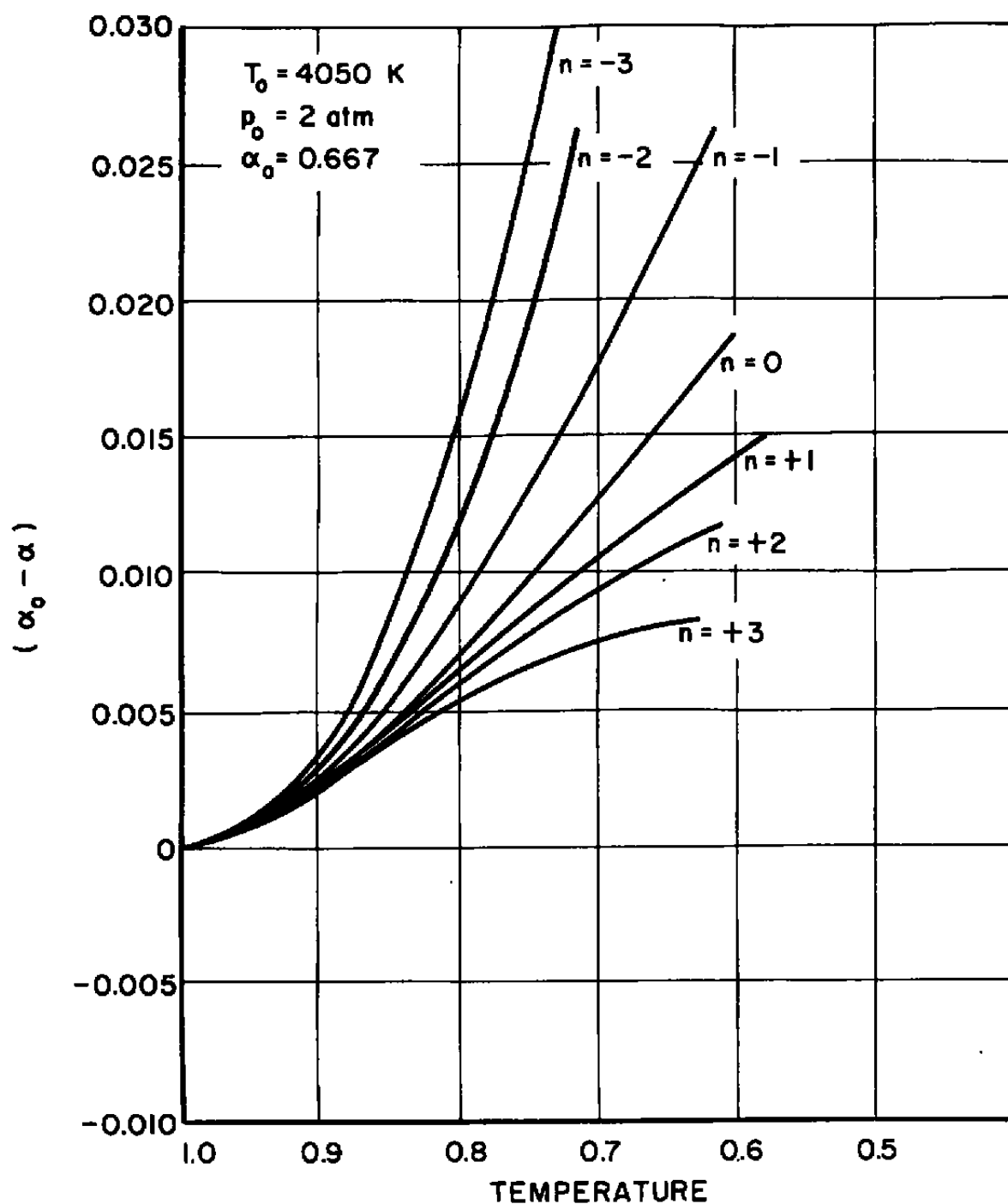


FIGURE 3-9 FLOW COMPOSITION, CASE II

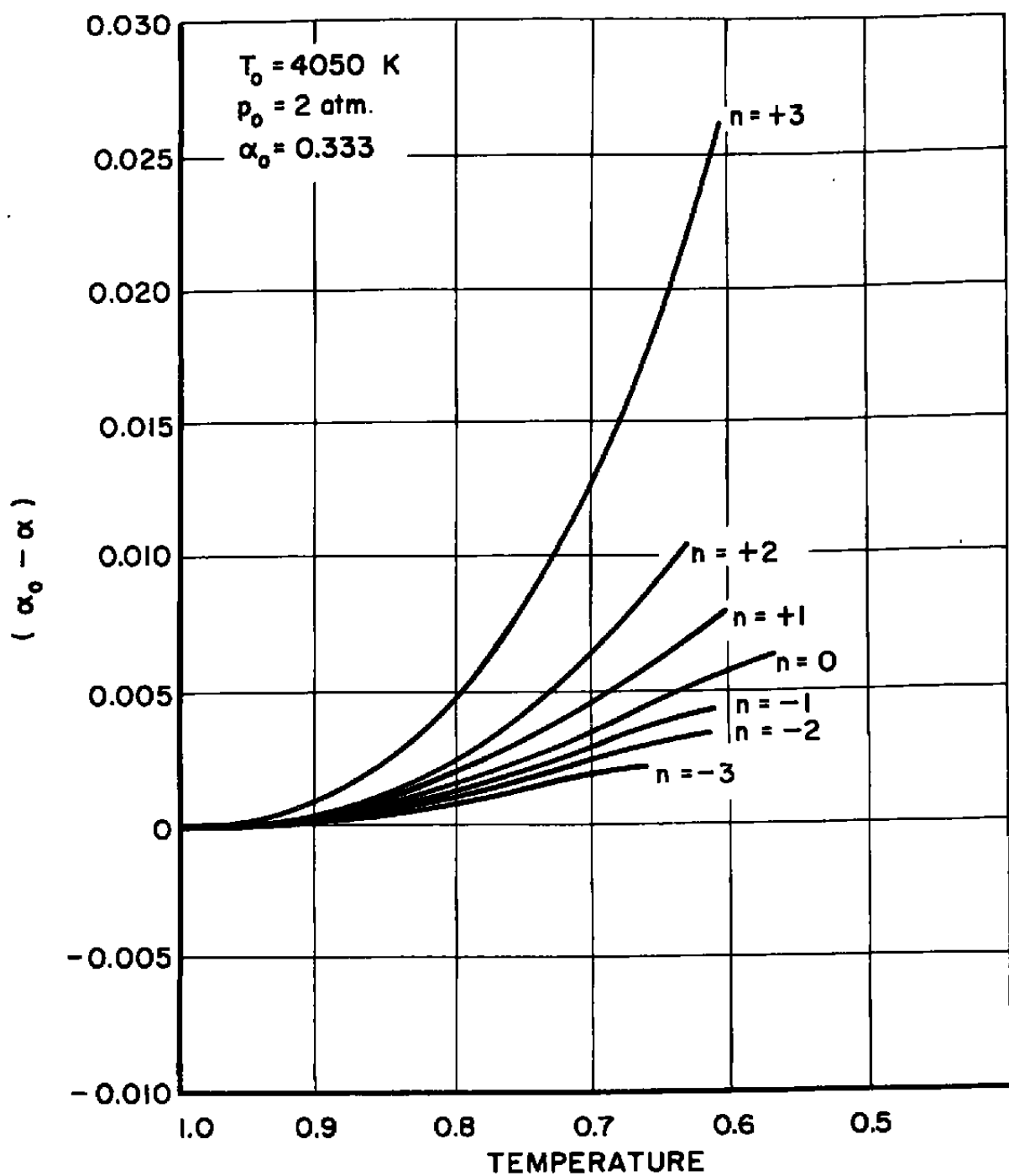


FIGURE 3-10 FLOW COMPOSITION, CASE III

molecular weight.

Surprisingly, deliberately starting at the throat with a non equilibrium composition has only a small, though pronounced, effect on the composition profiles. In part this is a result of the choice of the nozzle contour, since, in this case, the composition must start at the throat with a zero rate of change in all cases. Thus the nozzle throat may be considered to be at a state of pseudo frozen composition.

Negative exponents ($n < 0$) for the recombination rate produce a different class of solutions for the flow composition. Inspection of the reaction equation will provide some insight into this distinction. There are basically two terms in the reaction equation, one indicating the direction and extent to which the flow deviates from equilibrium and the other, containing the recombination rate function, indicating the speed with which the reaction will occur. For the case of $n > 0$ the rate of reaction term controls the change in composition, and since it decreases as the temperature decreases, the composition approaches a constant, or nearly constant, value quickly. For a negative value of n the rate of reaction term increases with decreasing temperature, thus having a tendency to increase the rate of change of composition.

The term indicating extent of the deviation from equilibrium in the reaction equation is in general a decreasing function with decreasing temperature (although initially its value may increase depending on the initial conditions), and at low temperatures the change in composition must approach zero. However, for the low pressures and pressure ratios considered here, the temperature does not decrease sufficiently

for this secondary effect to predominate. Unfortunately, the computer overloaded for temperatures of about 0.60 for negative n 's, and some minor rescaling of the problem would be necessary to obtain solution for greater temperature ratios.

The choice of nozzle contour is of particular significance in determining the composition. The linear nozzle studied here restricts the slope of the composition profile to zero at the throat. This effectively smooths out the composition change and decreases the effect of recombination rate on the flow variables. It is anticipated that other nozzles would give considerably different composition profiles, particularly for the cases in which the composition is not initially in equilibrium. However, the conclusions of this study should not be affected.

Figures 3-11, 3-12, and 3-13 compare the velocity, pressure, and area for the two extreme cases of recombination rate considered. As would be expected, the velocity increases more rapidly in the composition changes as a result of the dissociation energy being returned to the flow. This same effect accounts for the fact that, for a given temperature ratio, the area is considerably different for the two extreme cases. The result of this area increase also causes the pressure to drop more rapidly for the case with greater reaction (with respect to temperature). In terms of a given nozzle with a fixed area ratio, it can be seen that the exit pressure is approximately the same and the velocity is greater by approximately 5 per cent for the case of negligible reaction. However, there is 20 per cent more thermal energy remaining

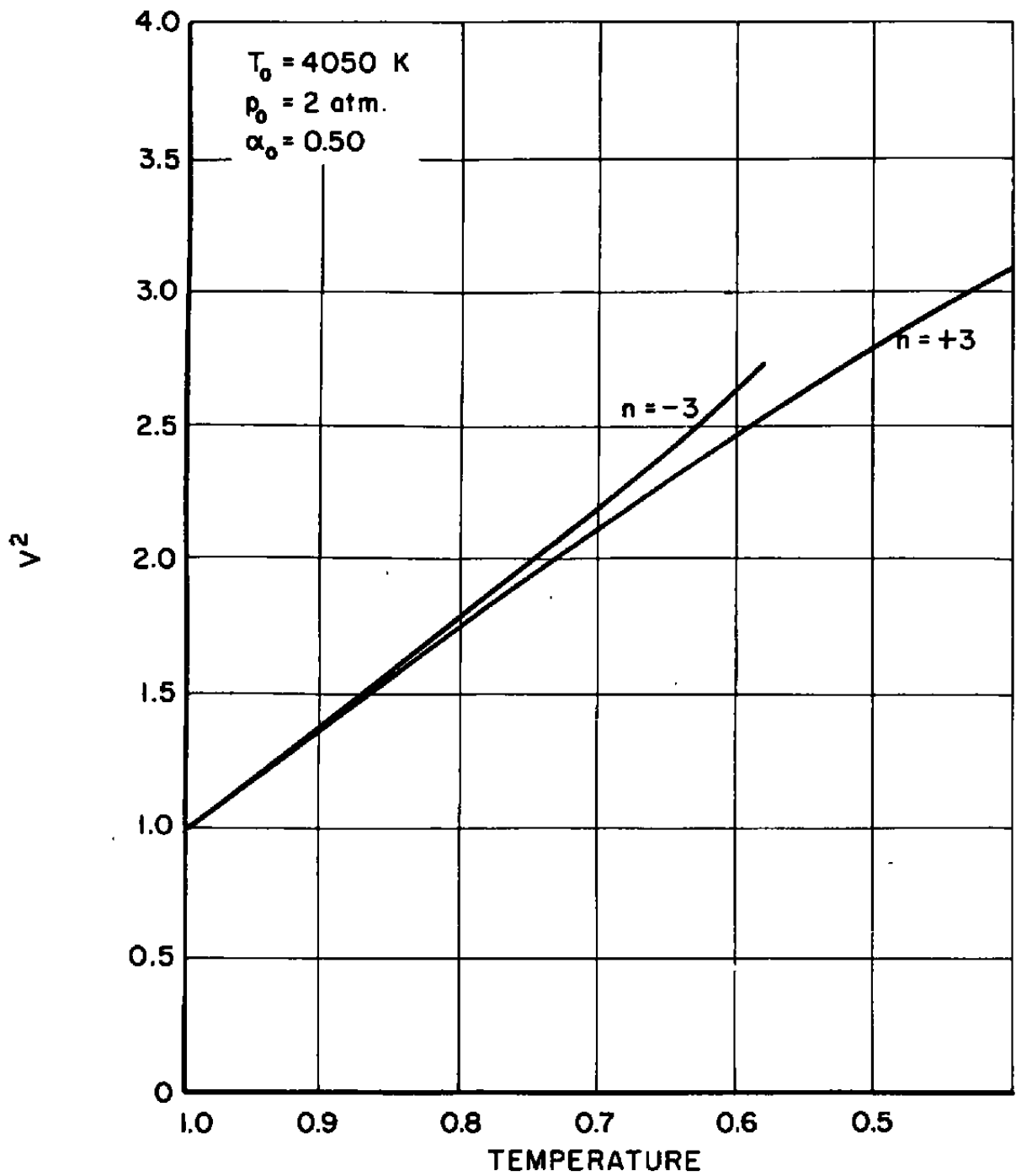


FIGURE 3-II FLOW VELOCITY

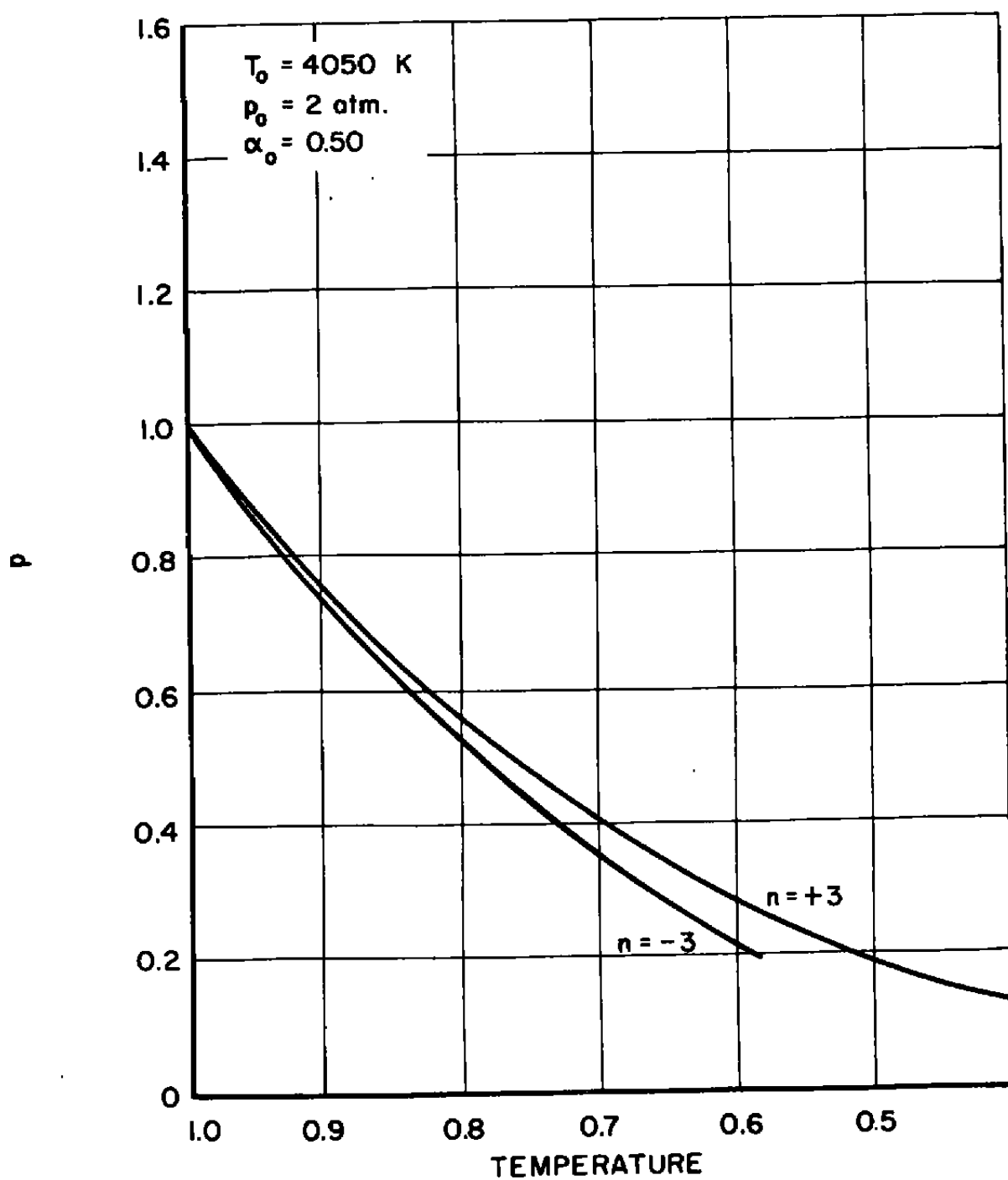


FIGURE 3-12

FLOW PRESSURE

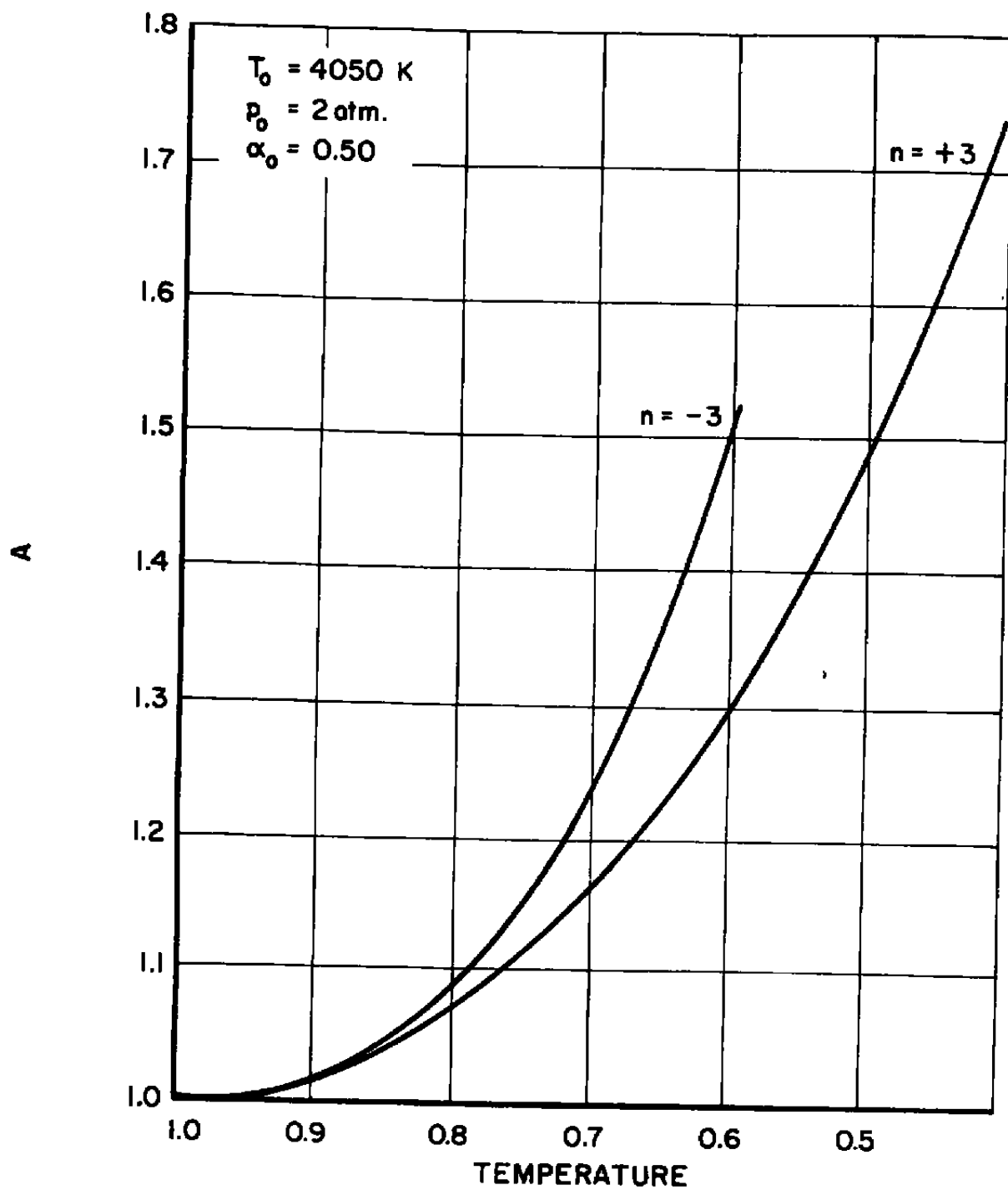


FIGURE 3-13

FLOW AREA

in the case of the more active mixture which could potentially be translated into kinetic energy. In terms of mach number, this difference in flow velocity would be considerably more pronounced, since it would include the temperature also.

All of the solutions obtained in this study with the exception of those presented in this section, are included in Appendix E, Results.

IV. CONCLUSIONS

The conclusions of this investigation may be summarized as follows:

1. The analog computer has been proven to be a versatile tool for examining the flow of a reacting gas. No major changes in the program used in this study would be necessary to examine the complete spectrum of possible boundary conditions.
2. Corrections to Lighthill's "ideal dissociating gas" are readily discernable but not of major importance.
3. The extent of reaction and shape of the composition profile is primarily determined by the form of the reaction rate law.
4. Reaction rates that increase with temperature have little effect on the flow composition (at low pressure) and such flows may be assumed to be frozen.
5. Reaction rates that decrease with temperature affect the composition significantly and in these cases the chemical reaction must be considered.
6. Initially non equilibrium compositions result in a greater or lesser change in composition, but this effect is coupled very closely to the particular nozzle contour considered.
7. The effect of form of the recombination rate on the flow of a reacting gas is significant and must be determined exactly before detailed analyses of potential applications can be made.

V. RECOMMENDATIONS FOR FUTURE INVESTIGATORS

The facility with which the set of equations describing the flow of a reacting gas suggests many additional areas of investigation.

1. The nozzle contour has a definite effect on the composition profile and a variety of contours should be considered. Unless considerably more computing equipment than was used in this study is available, this would necessitate using the considerably simplified model of a dissociating gas suggested by Lighthill.
2. The extension of the study of a dissociated gas flow to the study of either a purely ionized flow or even a partially dissociated and partially ionized flow is readily foreseeable. The greatest difficulty in this extension would be the availability of computer components. The reaction law is merely a simple loop and a variety of different forms or a series of different reactions can be added as separate circuits which can be included or excluded at predetermined points in the solution. In other words, several different mechanisms for the pertinent reactions, each significant for various pressures and temperatures, may be considered simultaneously. Bray (Reference 33) has considered this problem but along the lines of his studies on a dissociating flow, and his approach can only be considered a preliminary study.

3. The sensitivity of the composition profile to the recombination rate suggests that this may be a useful method for experimentally measuring the value of the recombination rate. Since the equilibrium constant is well known and the flow may be established for a reasonable period of time, the problem of measuring the dissociation rate and inferring the recombination rate is eliminated. The composition may be measured very precisely spectroscopically and the low pressures considered in this study are readily attainable in the laboratory.
4. Specific nozzle contours for particular applications can be designed as an extension of the current study. Particular relationships between the various parameters can be specified and the resulting nozzle contour determined. This analysis may well indicate better approaches for the measurement of recombination rate than that suggested above.
5. An analog computer also provides a convenient means for establishing discontinuities in a flow field by suddenly adding a step function (voltage). Therefore it would be convenient to use it for the study of the chemical reactions occurring behind a strong normal shock wave.
6. The speed of sound in a reacting mixture is a function of reaction rate and would lend itself to study in a manner similar to that applied here. In addition, the relationship between sonic velocity and the critical velocity at the nozzle throat could be examined.

APPENDIX A

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APPENDIX B

Nomenclature

English Symbols:

- A - flow area
- A - Helmholtz free energy (Chapter II)
- A_2 - typical diatomic molecule
- D - dimensionless constant (defined by Equation 2-15)
- E - dissociation energy
- F - Gibbs free energy (Chapter II)
- F - dimensionless recombination rate (defined by Equation 2-20)
- g - statistical weight of the electronic ground state
- G - dimensionless equilibrium constant (defined by Equation 2-21)
- h - Planck's constant
- H - enthalpy
- I - molecular moment of inertia
- J - dimensionless vibration function (defined by Equation 2-17)
- k - Boltzmann's constant
- k_D - dissociation rate
- k_R - recombination rate
- K_p - equilibrium constant based on partial pressures
- m - particle mass
- n - exponent for recombination rate
- N - Avogadro's number
- N - reciprocal of the flow area
- p - pressure
- Q - partition function
- r - streamline coordinate

R - universal gas constant

S - entropy

T - absolute temperature

v - velocity

V - total volume

Greek Symbols:

α - dissociation parameter (defined by Equation 2-5)

β - dimensionless constant (defined by Equation 2-12)

η - dimensionless constant (defined by Equation 2-13)

θ - dimensionless constant (defined by Equation 2-16)

ω - characteristic frequency of molecular vibration

ρ - mass density

σ - symmetry factor

Subscripts:

A - atomic species

D - dissociation

e - equilibrium

elect - electronic

M - molecular species

R - recombination

rot - rotational

trans - translational

vib - vibrational

O - reference condition

Superscript:

O - standard state of one atmosphere

APPENDIX C

Boundary Conditions

Table C-1 lists the values of the physical constants used in this study as well as selected properties of six diatomic gases. Although oxygen has been used for the specific solutions presented here, the dimensionless form of the equations allows some generalization of these results to fit other gases.

The choice of the initial temperature is difficult and depends upon the composition and pressure. More pertinent to this study than the initial temperature is how far the initial composition is from an equilibrium composition. Using the subscript oe to indicate the equilibrium composition at the initial pressure and temperature, the equilibrium constant function may be written as

$$G_e = \frac{\alpha_{oe}^2}{(1 - \alpha_{oe}^2)}$$

This equation thus defines the initial temperature, through the equilibrium constant, for any particular equilibrium composition and initial pressure.

Arbitrarily the value of α_{oe} has been chosen to be 0.50. The throat pressure has been chosen to be 2 atm., this low pressure was chosen so that the solutions could be applied to current laboratory systems, most of which have glass calming chambers upstream of the nozzle. For oxygen, the corresponding temperature is 4050K. Three different values of the actual initial composition are studied, one above and one below equilibrium and the equilibrium composition.

As discussed in Chapter II, there is considerable doubt as to the correct value of the recombination rate for oxygen. Examination

| Gas | M | E/k | $h\nu/k$ | $I \times 10^{10}$ | σ | ϵ |
|-----------------|------|--------------------|--------------------|--------------------|----------|------------|
| | | $^{\circ}\text{K}$ | $^{\circ}\text{K}$ | gm-cm^2 | | |
| H | 1.01 | 26,000 | | | | 2 |
| H ₂ | 2.02 | 52,000 | 6,320 | 0.46 | 2 | 1 |
| N | 14.0 | 56,500 | | | | 4 |
| N ₂ | 28.0 | 113,000 | 3,400 | 13.6 | 2 | 1 |
| O | 16.0 | 29,500 | | | | 5 |
| O ₂ | 32.0 | 59,000 | 2,270 | 19.2 | 2 | 3 |
| Cl | 35.5 | 11,400 | | | | 4 |
| Cl ₂ | 71.0 | 28,800 | 813 | 108 | 2 | 1 |
| Br | 80.0 | 11,400 | | | | 4 |
| Br ₂ | 160 | 22,800 | 465 | 343 | 2 | 1 |
| I | 127 | 8,950 | | | | 4 |
| I ₂ | 254 | 17,900 | 309 | 742 | 2 | 1 |

$$h = 6.62 \times 10^{-27} \text{ erg sec/particle}$$

$$N = 6.02 \times 10^{23} \text{ particles/gm-mole}$$

$$R = 8.31 \times 10^7 \text{ ergs/}^{\circ}\text{K gm-mole}$$

$$k = 1.38 \times 10^{-16} \text{ ergs/}^{\circ}\text{K particle}$$

$$l = \text{erg sec}^2/\text{gm cm}^2 = 1.01 \times 10^6 \text{ erg/cm}^3 \text{ atm}$$

TABLE C-1 Gas Parameters

of the recombination rate function, F , shows that the initial value of the recombination rate occurs as the product of $r_0 k_R(T_0)$ and that this is the only place that the characteristic length appears. Therefore, any change in the magnitude of the recombination rate at T_0 can be exactly compensated for by redefining the value of r_0 . The result is that only the temperature dependence of the recombination rate function need be considered. The value of F_0 has been chosen to be unity, a value that corresponds to $r_0 = 1.07$ cm and $k_R(T_0) = 8.4 \times 10^{14} (T_0/3500)^2 \text{ cm}^6 \text{ gm-mole}^{-2} \text{ sec}^{-1}$ (the value predicted by Matthews in Reference 34). Seven integer values of the temperature exponent in the recombination rate were considered, $-3 \leq n \leq +3$. Table C-2 summarizes the initial conditions.

The critical value of the velocity, V_0 , is difficult to calculate. However, for the computer it is very simple to determine its value on a trial and error basis, since it appears only twice as a coefficient and, as a result of the particular nozzle contour chosen, only one of these coefficients is initially important. Therefore, β is set by adjusting its value until the derivative of the area is zero, the criterion for the nozzle throat.

| | |
|------------------------|------------------|
| $P_o = 2 \text{ atm.}$ | $Q_o = 0.333$ |
| $\alpha_{os} = 0.500$ | $\theta = 0.560$ |
| $T_o = 4050 \text{ K}$ | $D = 14.6$ |
| $F_o = 1.00$ | $J_o = 1.33$ |

| CASE | α_o | η |
|------|------------|--------|
| I | 0.500 | 0.667 |
| II | 0.667 | 0.600 |
| III | 0.333 | 0.750 |

| SUBCASE | n |
|---------|----|
| A | +3 |
| B | -3 |
| C | +2 |
| D | -2 |
| E | +1 |
| F | -1 |
| G | 0 |

TABLE C-2 Initial Conditions

APPENDIX D

Analog Computer Program

The active element analog computer, or electronic differential analyzer, consists of a collection of high gain voltage amplifiers, resistors, capacitors, and servometers arranged in such a configuration that the voltages throughout the circuit behave identically as the physical parameters in the differential equations being solved. The circuit is set up by combining a number of integrators, summers, and multipliers in a closed loop such that the operations on the voltages correspond to those required by the differential equation.

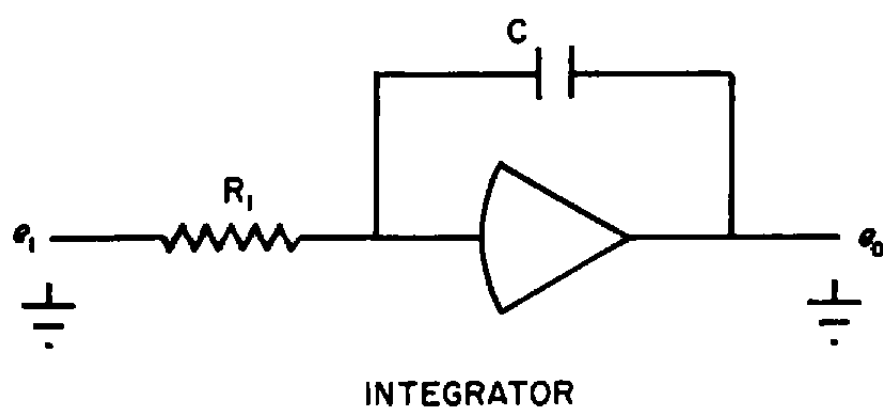
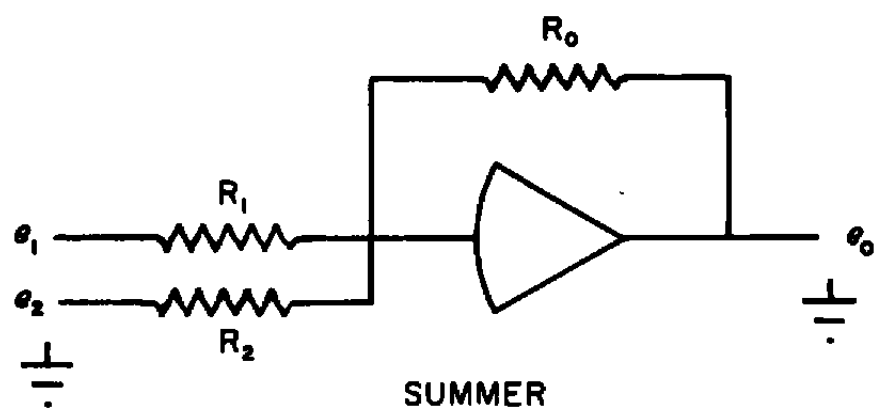
The basic element of the analog computer is a high gain (approximately 1,000,000) amplifier. This amplifier has the characteristic of inverting the sign of the voltage being amplified and may be assumed to have a negligible current flow through it. Figure D-1 shows how this unit coupled with series input resistances and either a feedback resistance or capacitance can be used to add or integrate a voltage. Initial conditions are set by imposing an initial voltage on the capacitor. Application of Kirchhoff's laws to the circuit of the summer results in the output voltage being equal to

$$e_o = - \frac{R_o}{R_1} e_1 - \frac{R_o}{R_2} e_2 + \frac{1}{A} \left[1 - e_o \left(\frac{R_o}{R_1} + \frac{R_o}{R_2} \right) \right]$$

If the amplifier gain, A , is large enough this may be approximated by

$$e_o = - \frac{R_o}{R_1} e_1 - \frac{R_o}{R_2} e_2$$

A similar analysis of the integrator and a similar approximation shows that, in this case,



BASIC COMPUTER COMPONENTS

FIGURE D-1

$$e_o = \frac{1}{CR_1} \int_0^t e_i dt$$

The most significant feature of these two results is that the amplifier characteristics do not appear and the gain of the circuit is a function only of the external electrical components.

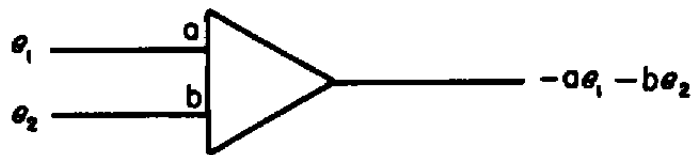
Another basic component used in analog computers is the servo-multiplier. This unit consists of a number of circular potentiometers driven by a servomotor. One of the potentiometers is connected to a reference supply and feeds its output back to the servomotor. The servomotor positions itself so that the input voltage is just balanced by this feedback voltage. In other words, each follow up potentiometer is positioned so that its output is decreased in proportion to the ratio of the servomotor driving voltage to the reference voltage. Thus, one function may be multiplied by as many other functions as there are follow up potentiometers. Multiplication by a constant coefficient is accomplished by feeding the voltage through a potentiometer and tapping off the required percentage. This constant coefficient must therefore always be less than unity.

Figure D-2 shows the computer symbols used in this report. Figure D-3 shows a number of basic configurations used to perform a number of common operations. Solving for e_o in the division circuit

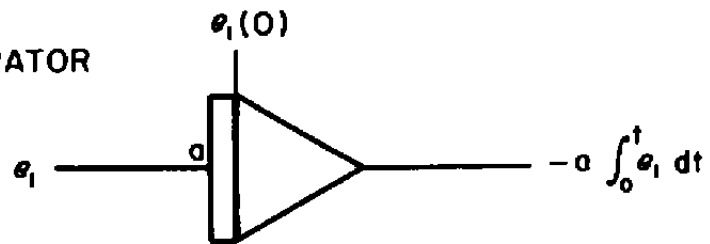
$$e_o = -100 \frac{e_1}{e_2} - \frac{100}{A} \frac{e_o}{e_2}$$

If the amplifier gain is sufficiently high, the second term can be

SUMMER



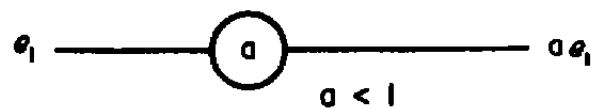
INTEGRATOR



SERVOMULTIPLIER



POTENTIOMETER



REFERENCE VOLTAGE

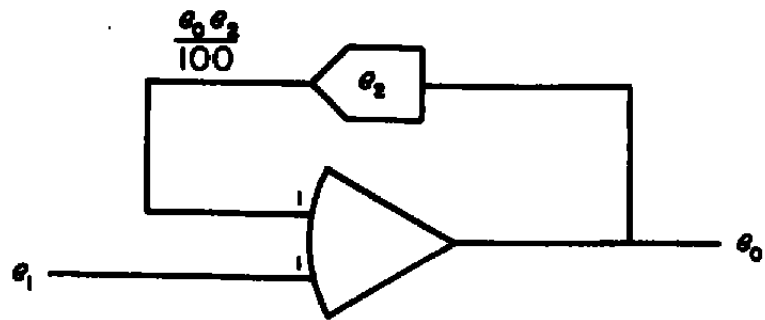


TIE POINT

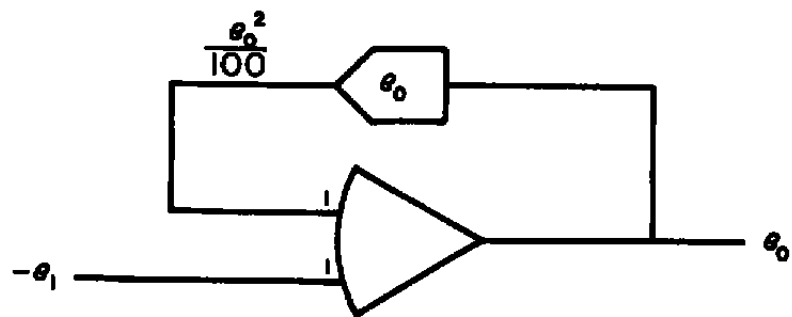


COMPUTER SYMBOLS

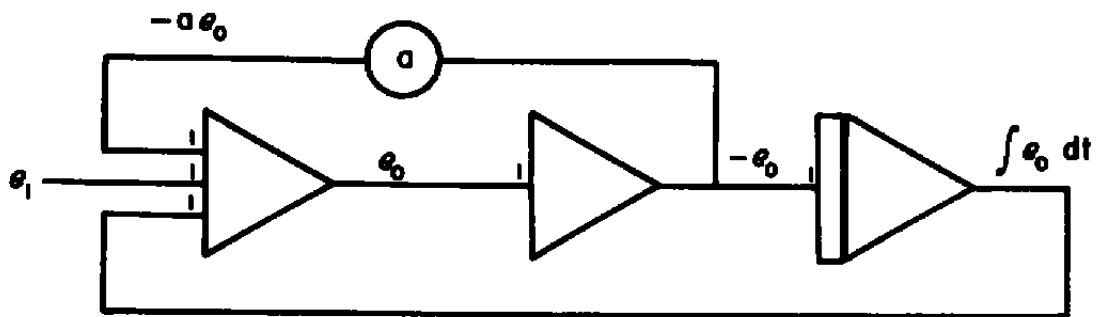
FIGURE D-2



DIVISION



SQUARE ROOT



DIFFERENTIATION

BASIC COMPUTER CONFIGURATIONS
FIGURE D-3

neglected and

$$e_o = -100 \frac{e_1}{e_2}$$

Similarly, for the square root circuit

$$e_o = 100 \sqrt{e_1}$$

The differentiation circuit is only an approximation and, as such, is generally not recommended. Solving for the value of e_o .

$$e_o = \frac{de_1}{dt} + (1-a) \frac{de_o}{dt}$$

For values of a approaching unity, this expression approximates the derivative more closely.

The electronic analog computer may be used to solve a variety of engineering problems (see References 35-38). It is best suited for solving systems of ordinary differential equations describing initial condition problems; however, it may be used on non initial condition problems or even some partial differential equations.

A number of factors must be carefully considered in preparing a problem for solution on a computer. As evidenced by the previous discussion, the independent variable for the computer is time, and all of the dependent variables are voltages. This necessitates scaling of all of the physical variables in terms of voltages. Most computer components are designed to operate linearly for voltages between 0 and ± 100 volts. Therefore all the variables should be scaled so that their absolute value is less than 100 volts throughout the entire solution.

(The FACE computers used in this study have an automatic overload indicator to stop the solution if at any time any voltage exceeds 100 volts.) In order to minimize errors, it is desirable to keep the voltages as large as possible, particularly in subtraction operations. Scaling the time for the solution presents different considerations. Long times allow errors to accumulate as a result of amplifier drift, capacitor leakage, etc., whereas short times produce errors, since the capacitors have their inherent time constants and the servomultipliers will track satisfactorily up to approximately 1 cps. (For faster solutions non-mechanical electronic multipliers may be used, but they are less dependable and less accurate than servomultipliers.)

The form of the equations and the sequence of operation is of considerable importance in their solution. Ideally, the equations should be cast in a self-compensating form, that is, for a decreasing function the derivative should be equal to the negative of the variable times a positive function. This formulation has a tendency to correct itself in that if the variable is too large, it corrects itself by adjusting the derivative to compensate. Effectively this approach forces all errors to oscillate around the proper solution rather than continually increase as the solution progresses. A serious difficulty occurs if the problem involves the difference of two values of nearly equal magnitude. In addition to the fact that small errors are magnified in this operation, the character of the solution may change radically if the error is sufficient to change the algebraic sign of the result. This latter difficulty may be removed if the nature of the problem is such

that the correct sign for this small voltage is known. In this case the result may be forced to be correct by feeding it through a diode or by driving a servomultiplier and allowing it to respond in one direction only. Inspection of the division circuit shows that the accuracy is seriously affected if the divisor is a very small number, even though the quotient may be less than 100 volts.

The set of eight simultaneous differential equations describing this problem of a reacting nozzle flow have been set up for the computer solution and are presented in Chapter III. Inspection of these equations shows that they are self compensating as much as possible. The reaction equation contains the difference between two nearly equal quantities, the difference between them being positive or negative depending upon the deviation from equilibrium, and also, the area function starts at zero and then increases. The final program is shown in Figures D-4A and D-4B. Inspection shows how these problems were circumvented in this case. The area function, $1/N \, dN/dt$, drives a servomultiplier, allowing only negative values, since the solution starts at the nozzle throat where this function is identically zero. The difference between the two nearly equal quantities has not been adjusted, other than maximizing the voltages, primarily as a result of lack of computer components. The choice of the reciprocal of the area, N , as a computer variable was made to formulate a self compensating equation as well as giving it a maximum value at the beginning of the solution. The choice of p/T as a variable was made to reduce the rate of change of pressure and give more accurate results. The choice of $dT/dt = -T^2$

for the independent variable function was made to minimize the number of computer components necessary for the problem solution. Nevertheless, this problem required the following components

- 8 - Integrators
- 24 - Summing Amplifiers
- 8 - Servomultipliers
(18-separate multiplier circuits)
- 27 - Potentiometers
- 2 - Switches

Figure D-5 is a reproduction of a sample solution to the set of differential equations. It is the output of a six channel Sanborn Recorder. Despite the fact that the program has been optimized to minimize error and the actual components, resistors and capacitors, are accurate to 0.1 per cent and enclosed in a thermostatically controlled oven, errors will accumulate and must be checked. Although a complete error analysis is out of the question for a problem this complex, a very good check on the accuracy is afforded through the fact that the equation of state may be integrated. In other words, the error is a direct function of how close the following identity is satisfied

$$\frac{p}{T} \frac{AV}{\eta(1+\alpha)} = 1$$

Figure D-6 shows how closely the solutions obtained in this study satisfy this restriction. The curve presented represents the average of a number of solutions. Comparison with Figure D-5 shows that the accuracy is well within the limits with which the computer output can be read. The sharp increase in error at the lower temperatures is caused by the small

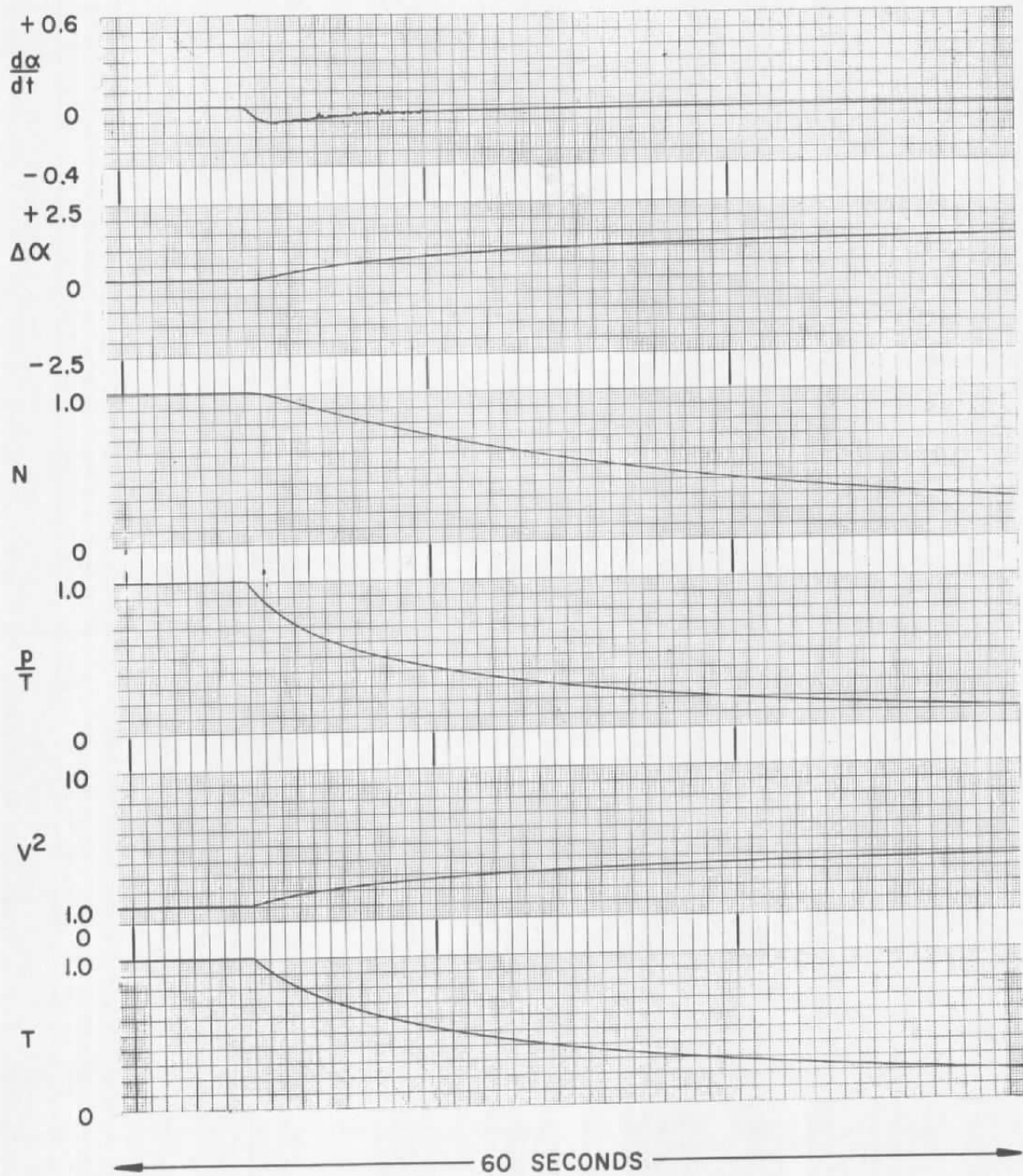


FIGURE D-5 SAMPLE SOLUTION

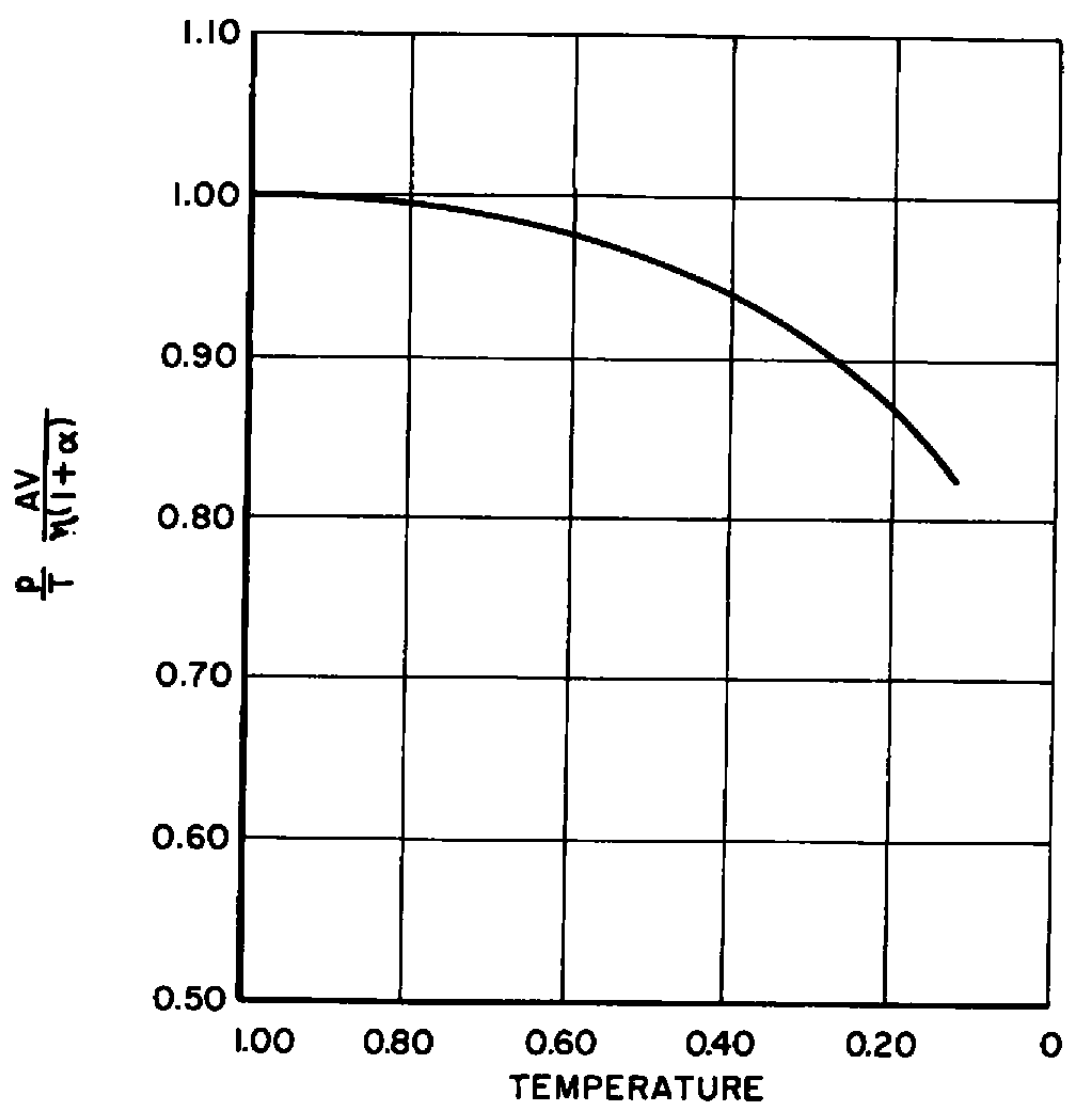
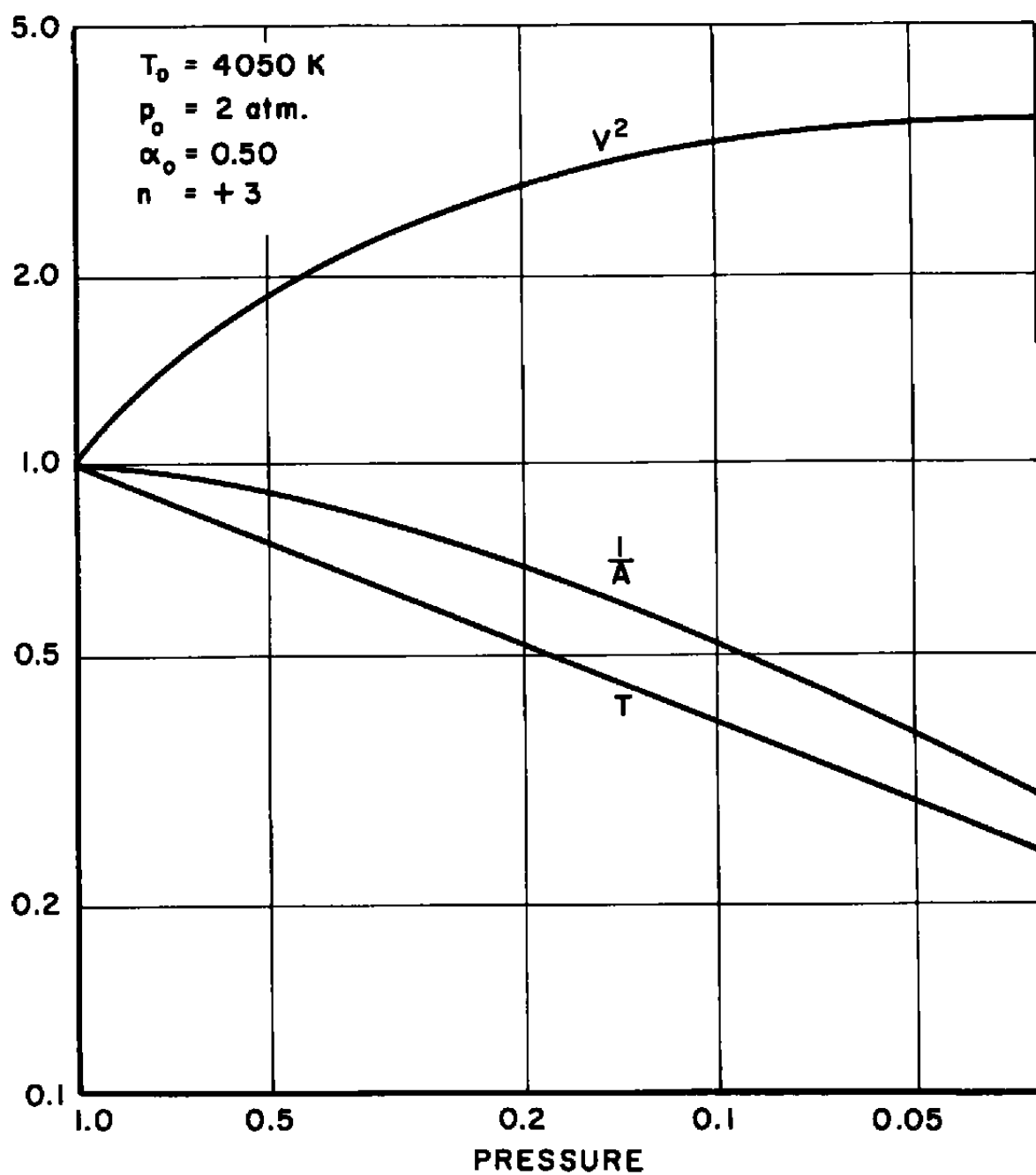


FIGURE D-6 TYPICAL ERROR

values of most of the parameters and the resulting inaccuracy of reading the data. However, since the major interest is centered upon the initial portion of the solution, this presents no major problem.

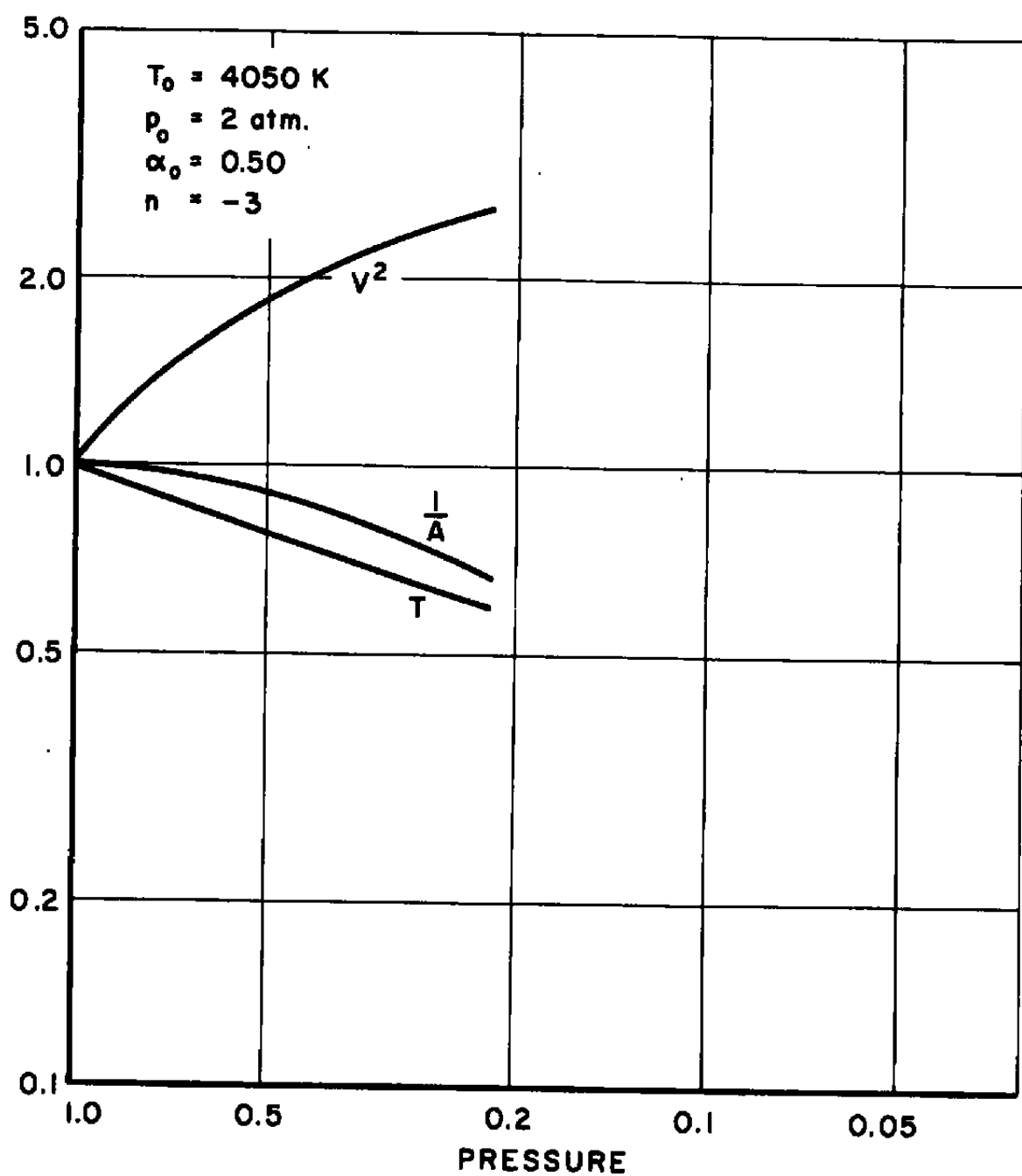
APPENDIX E

Computer Solutions



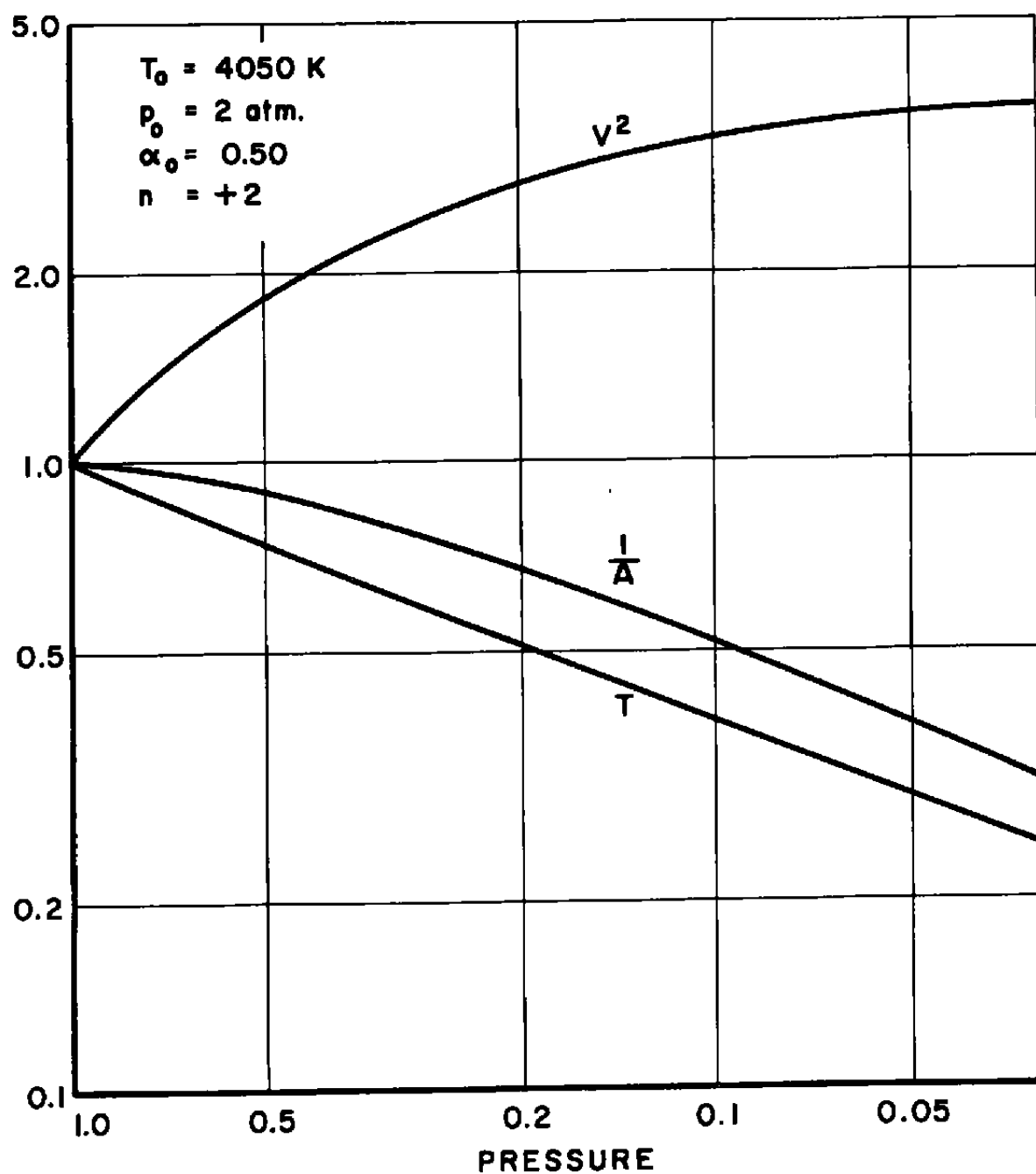
NOZZLE FLOW PARAMETERS, CASE IA

FIGURE E-1



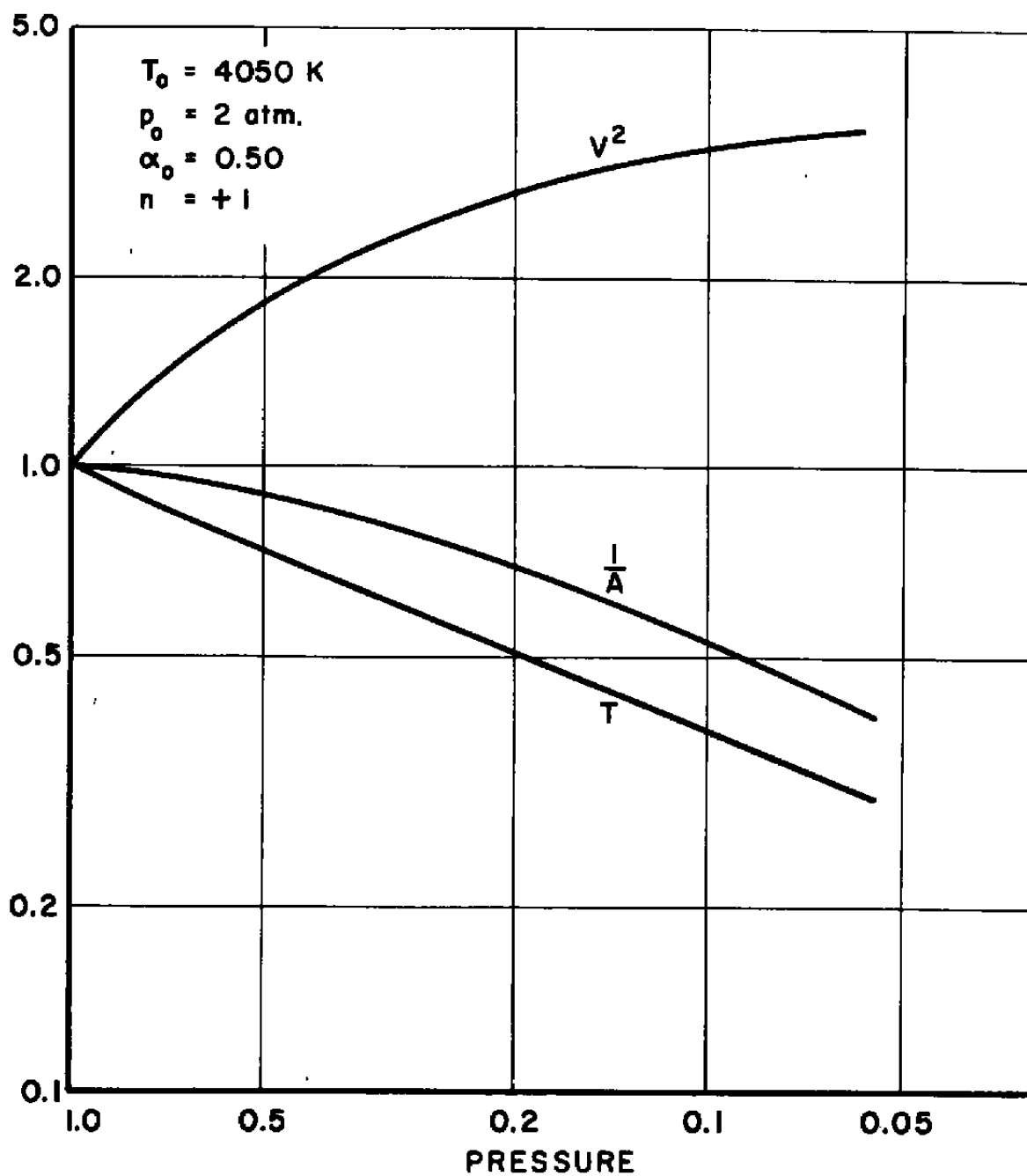
NOZZLE FLOW PARAMETERS, CASE IB

FIGURE E-2



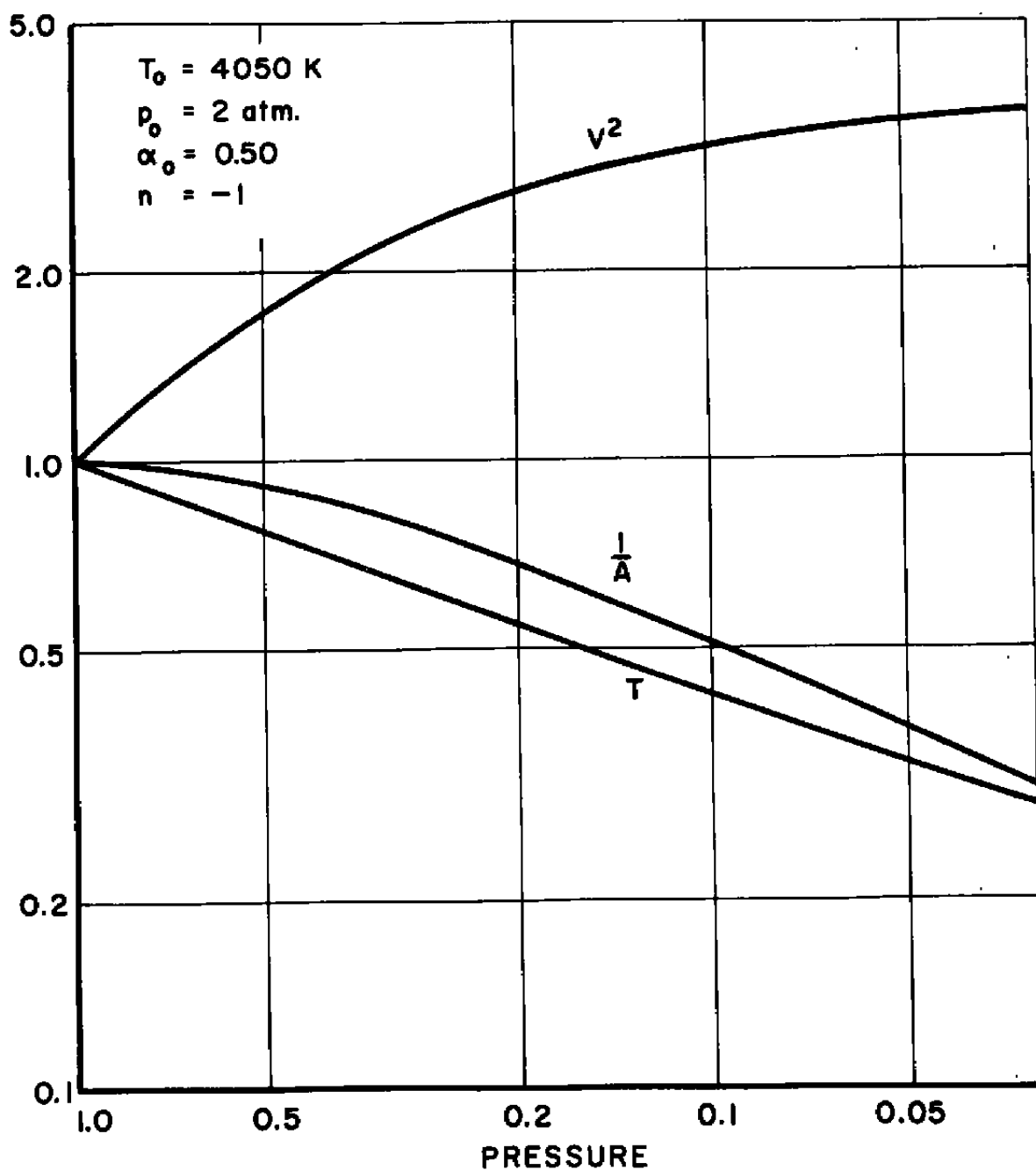
NOZZLE FLOW PARAMETERS, CASE IC

FIGURE E-3



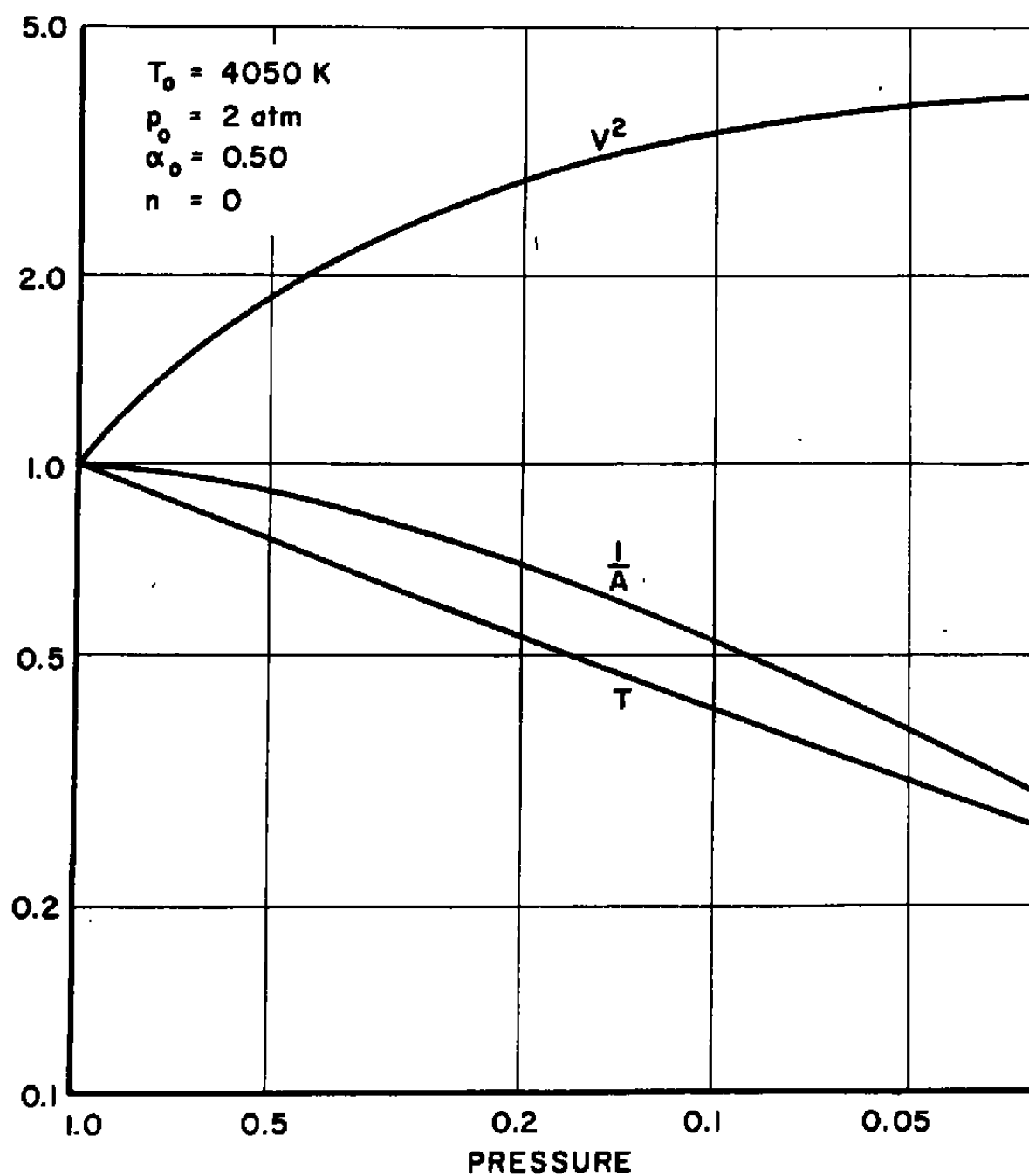
NOZZLE FLOW PARAMETERS, CASE IE

FIGURE E-4



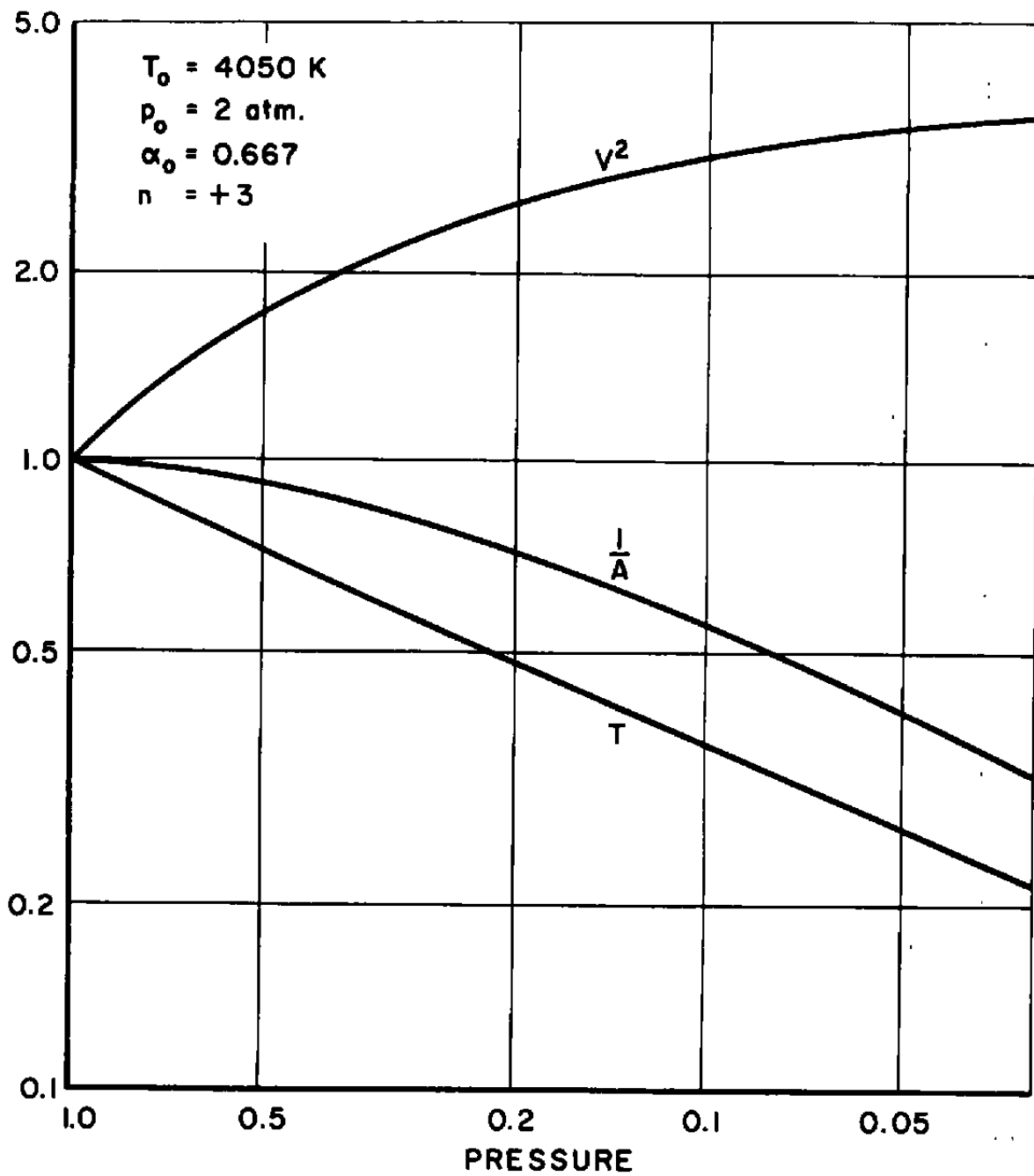
NOZZLE FLOW PARAMETERS, CASE IF

FIGURE E-5



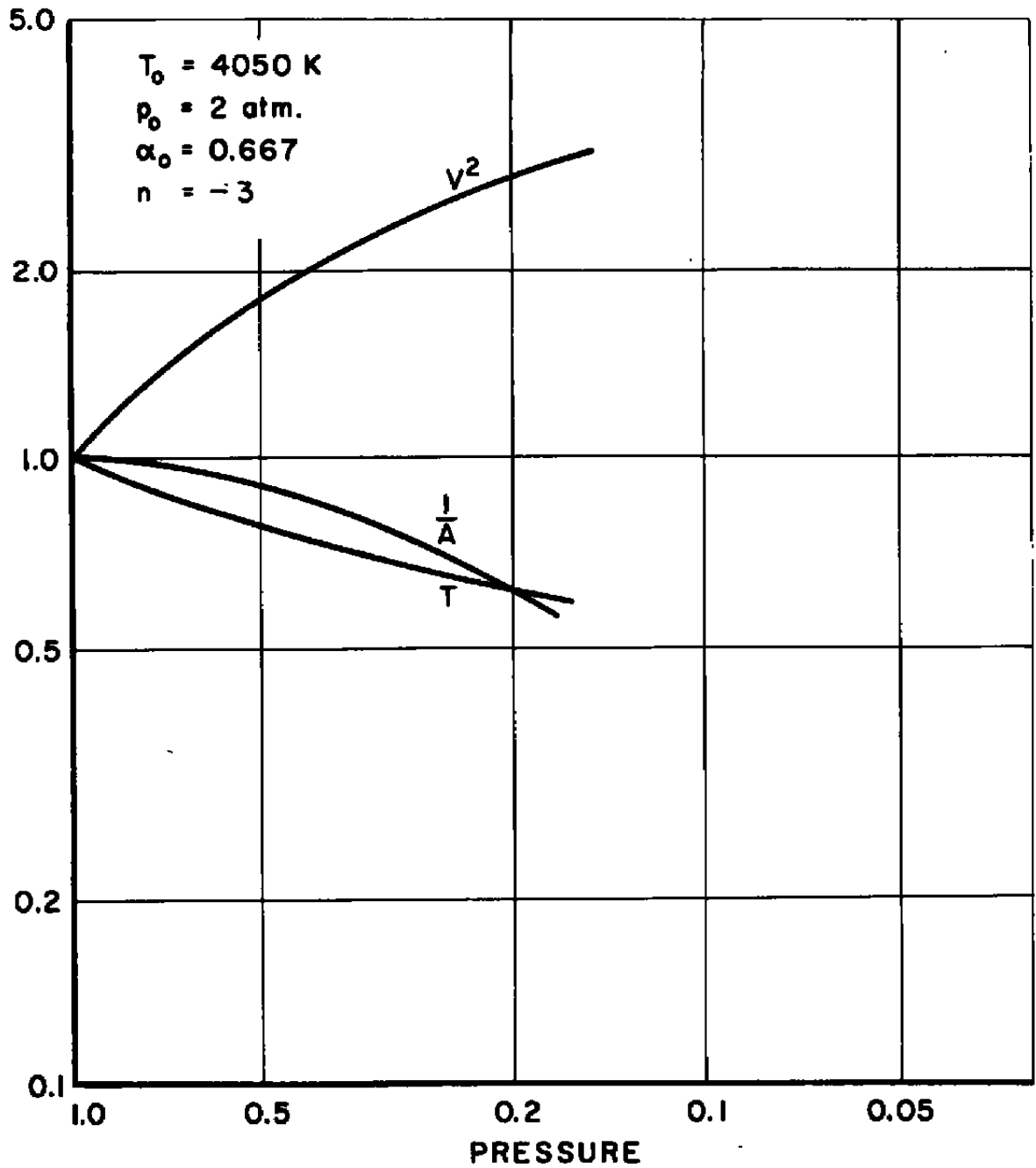
NOZZLE FLOW PARAMETERS, CASE IG

FIGURE E-6



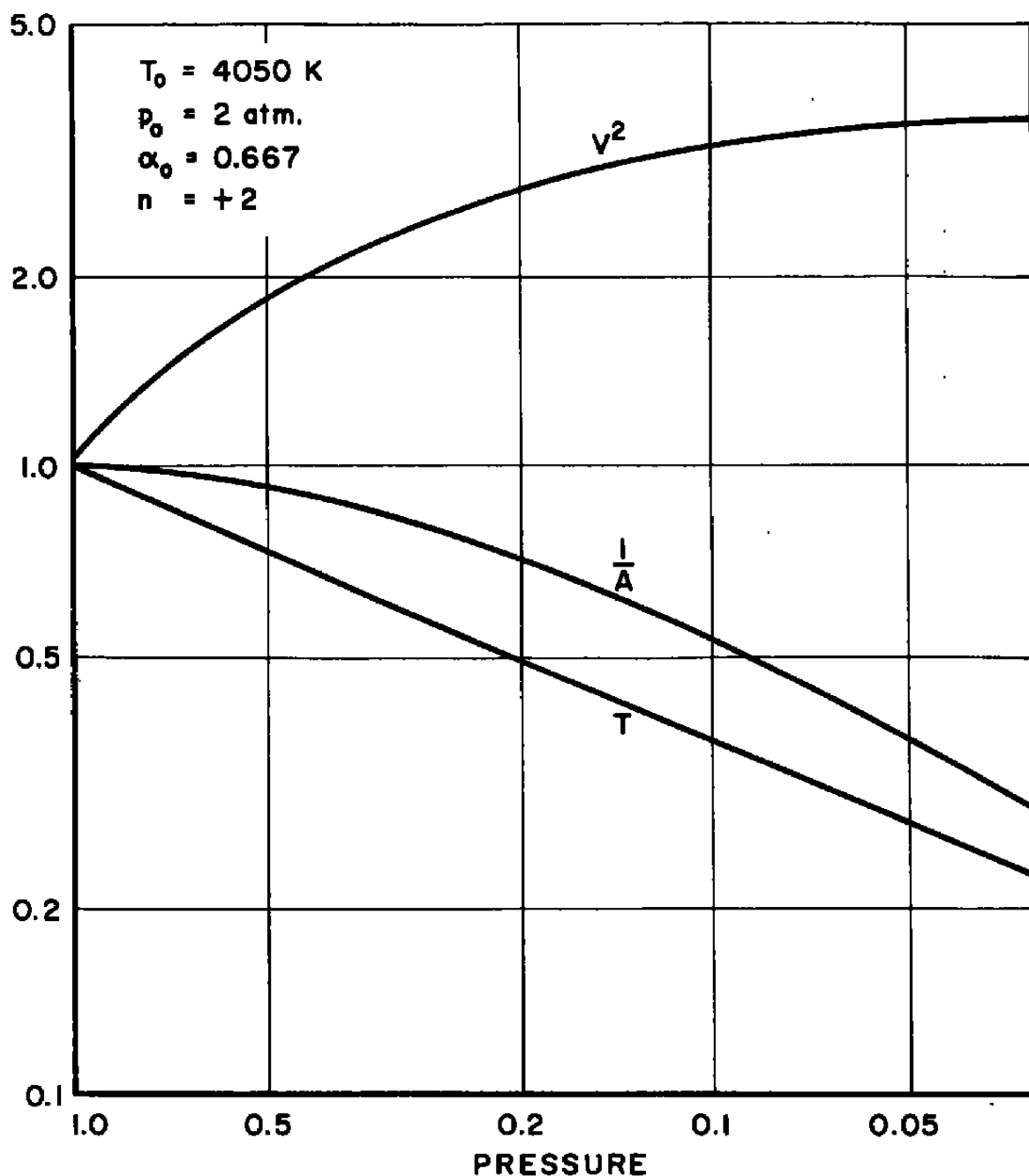
NOZZLE FLOW PARAMETERS, CASE II A

FIGURE E-7



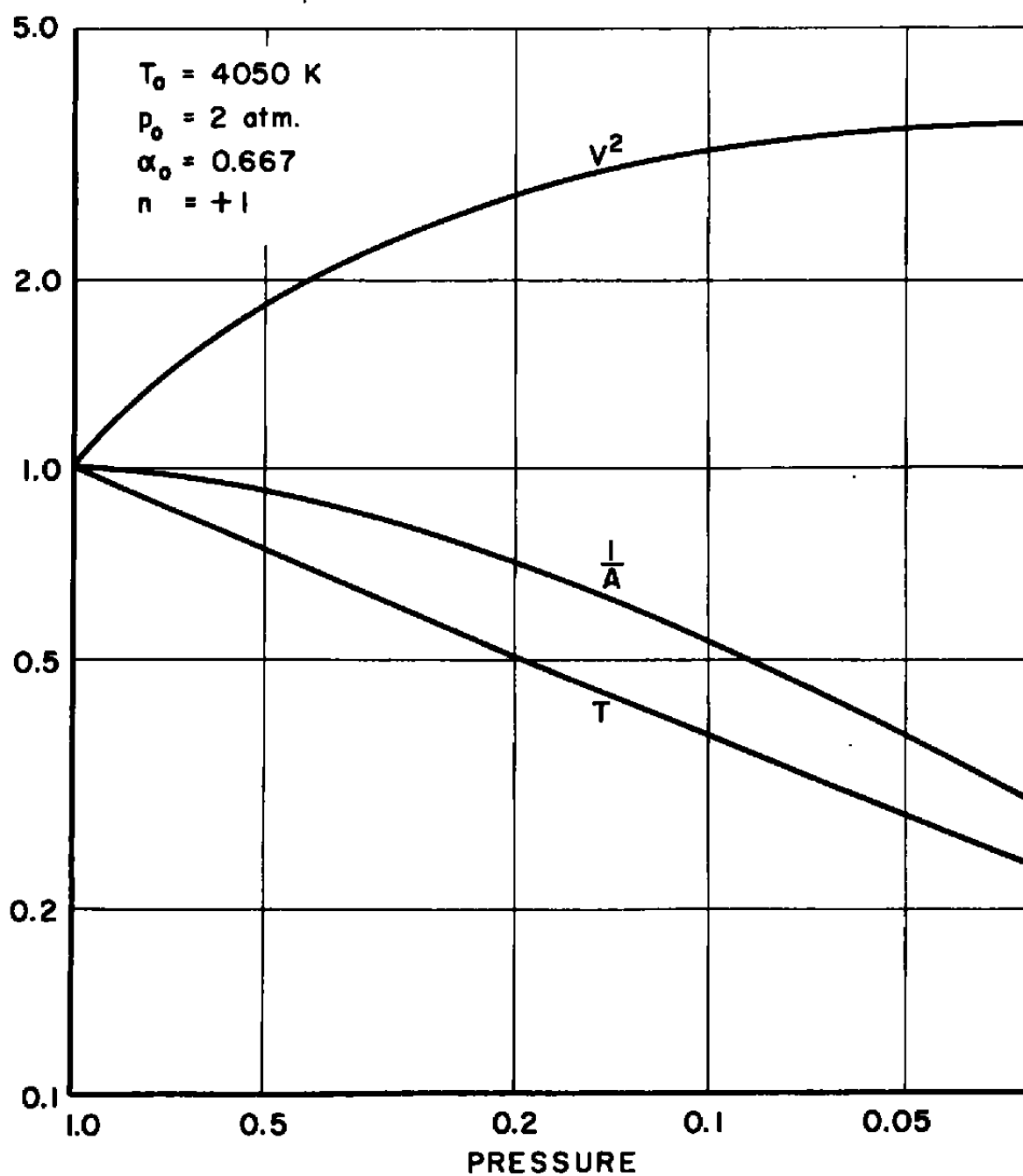
NOZZLE FLOW PARAMETERS, CASE II B

FIGURE E-8



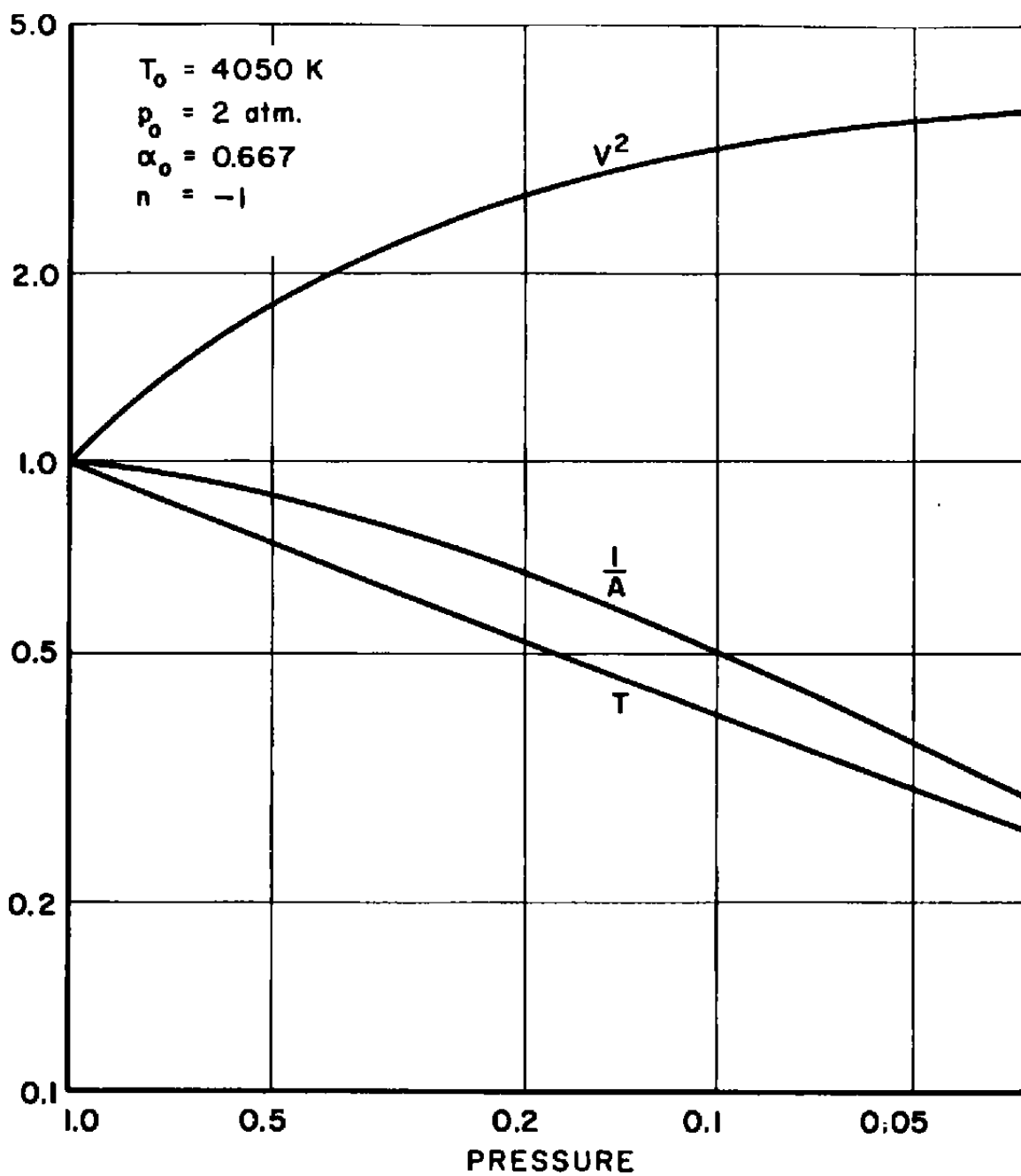
NOZZLE FLOW PARAMETERS, CASE II C

FIGURE E-9



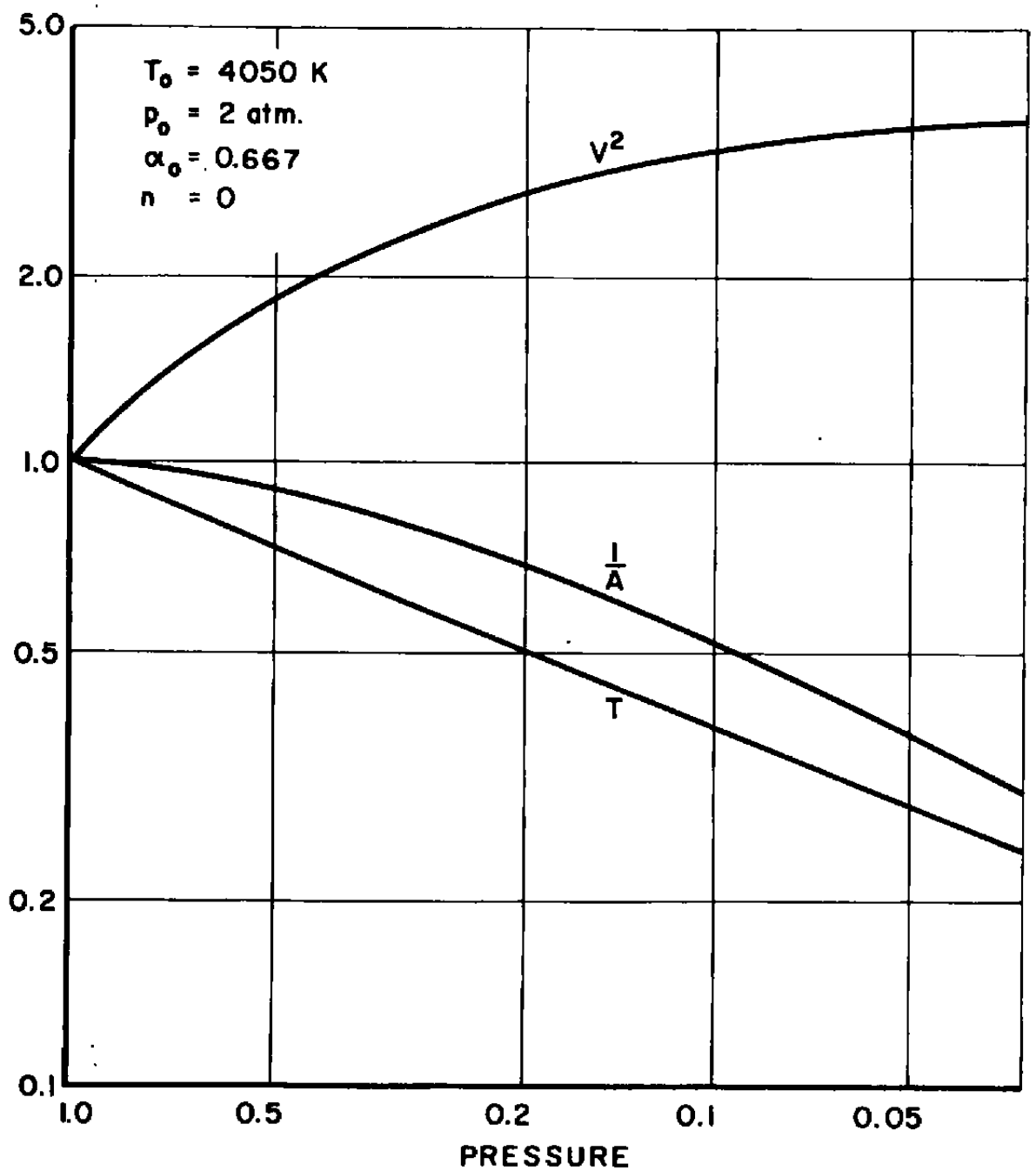
NOZZLE FLOW PARAMETERS, CASE II E

FIGURE E-10



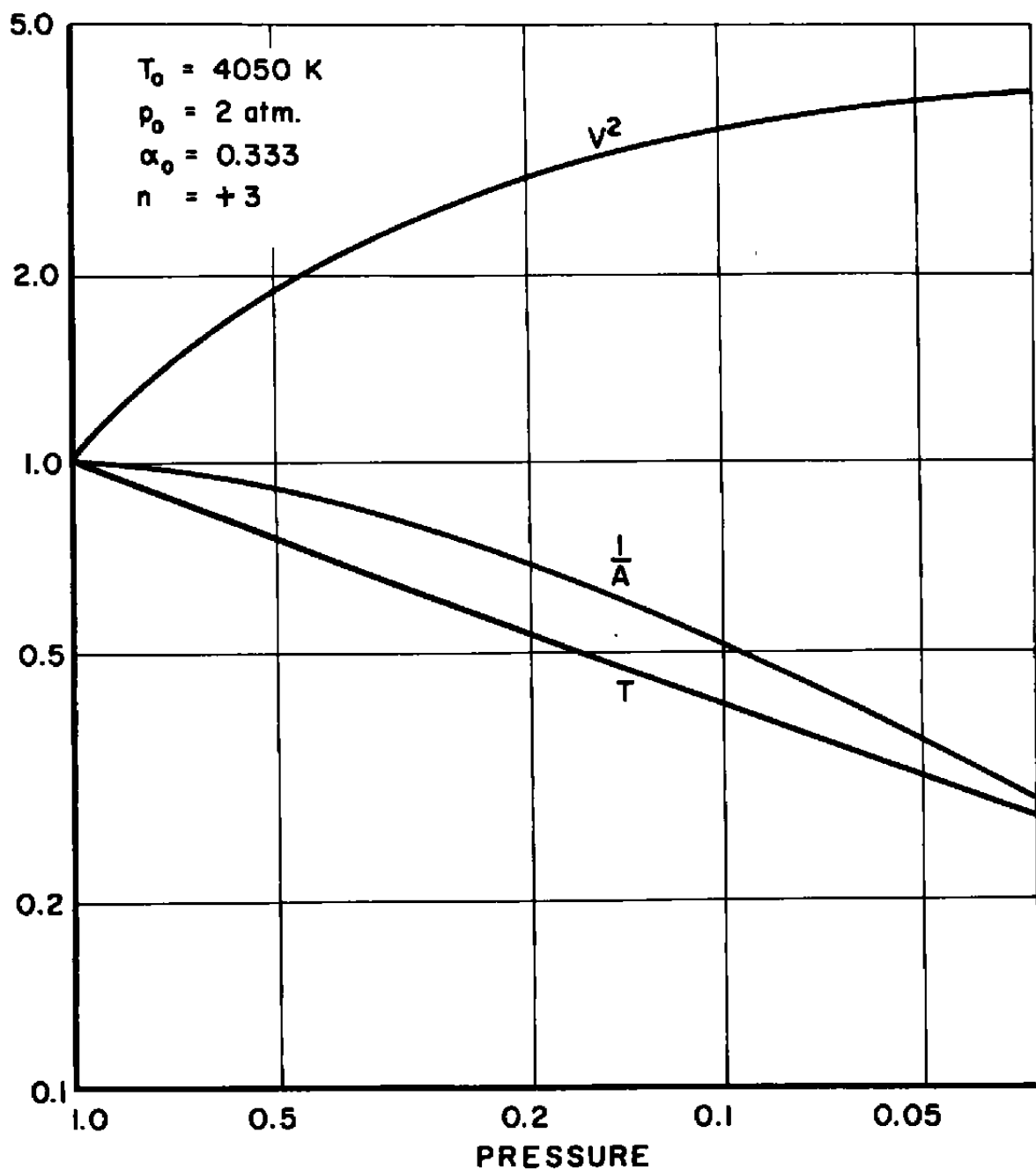
NOZZLE FLOW PARAMETERS, CASE IIF

FIGURE E-II



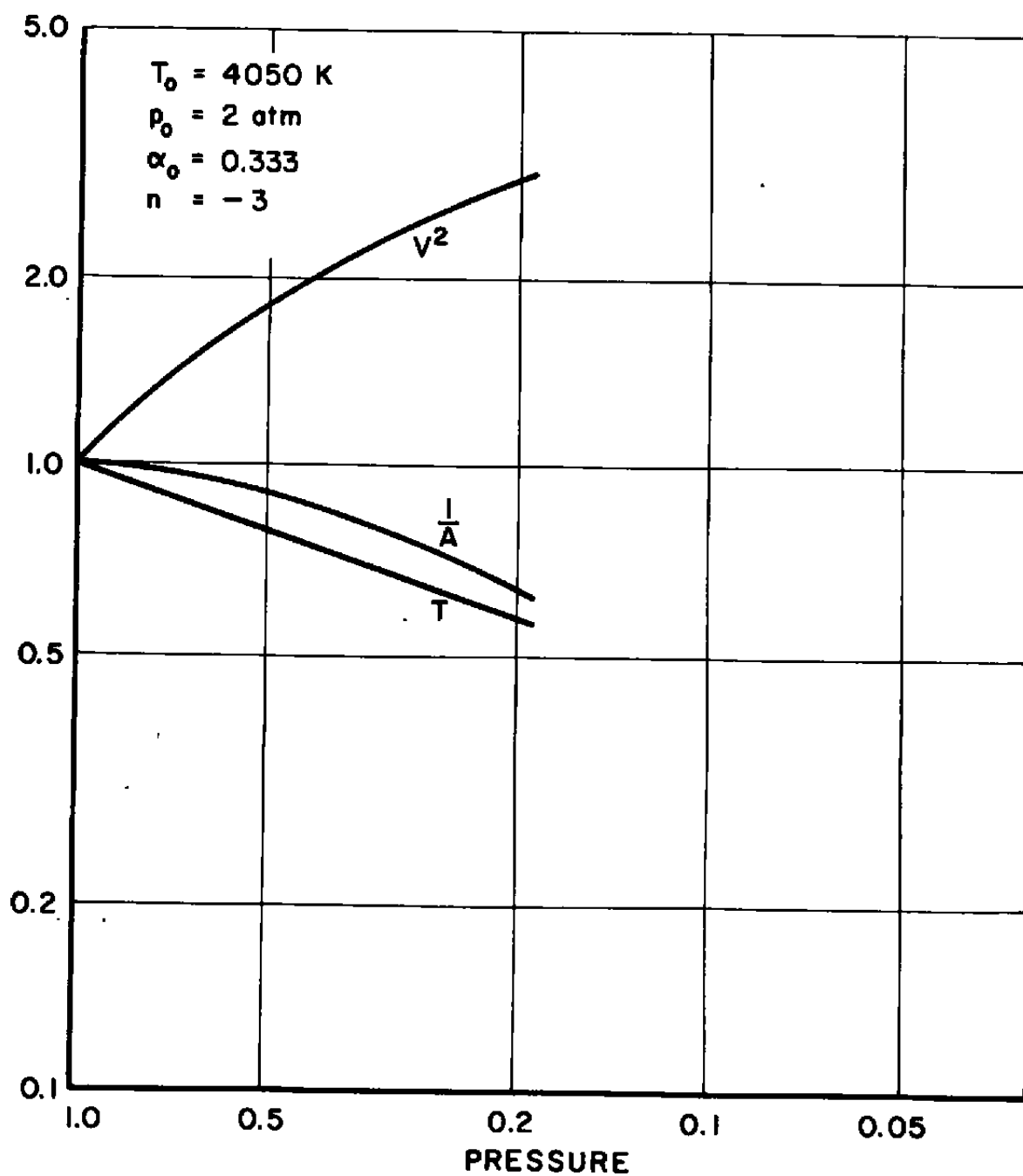
NOZZLE FLOW PARAMETERS, CASE II G

FIGURE E-12



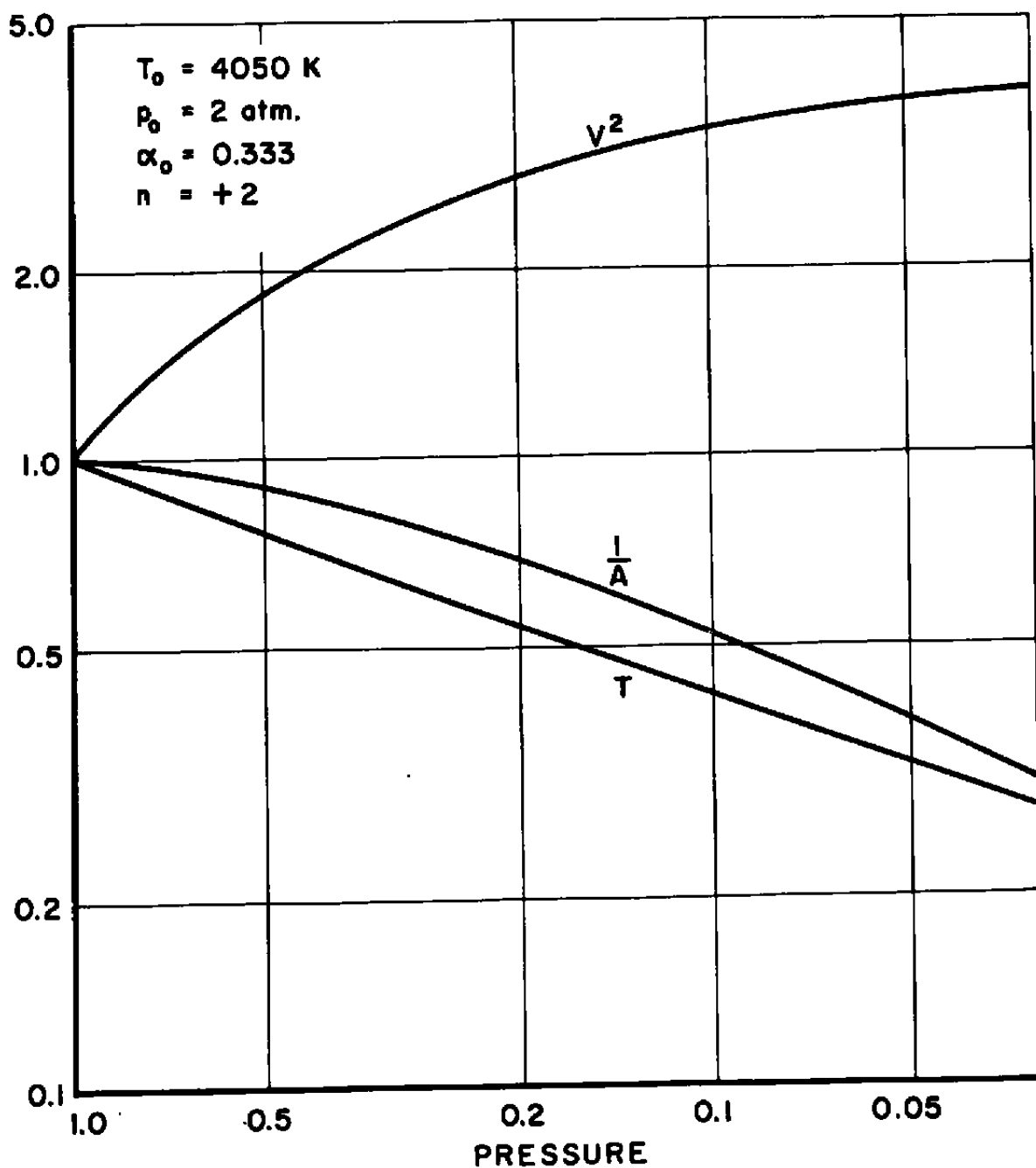
NOZZLE FLOW PARAMETERS, CASE IIIA

FIGURE E-13



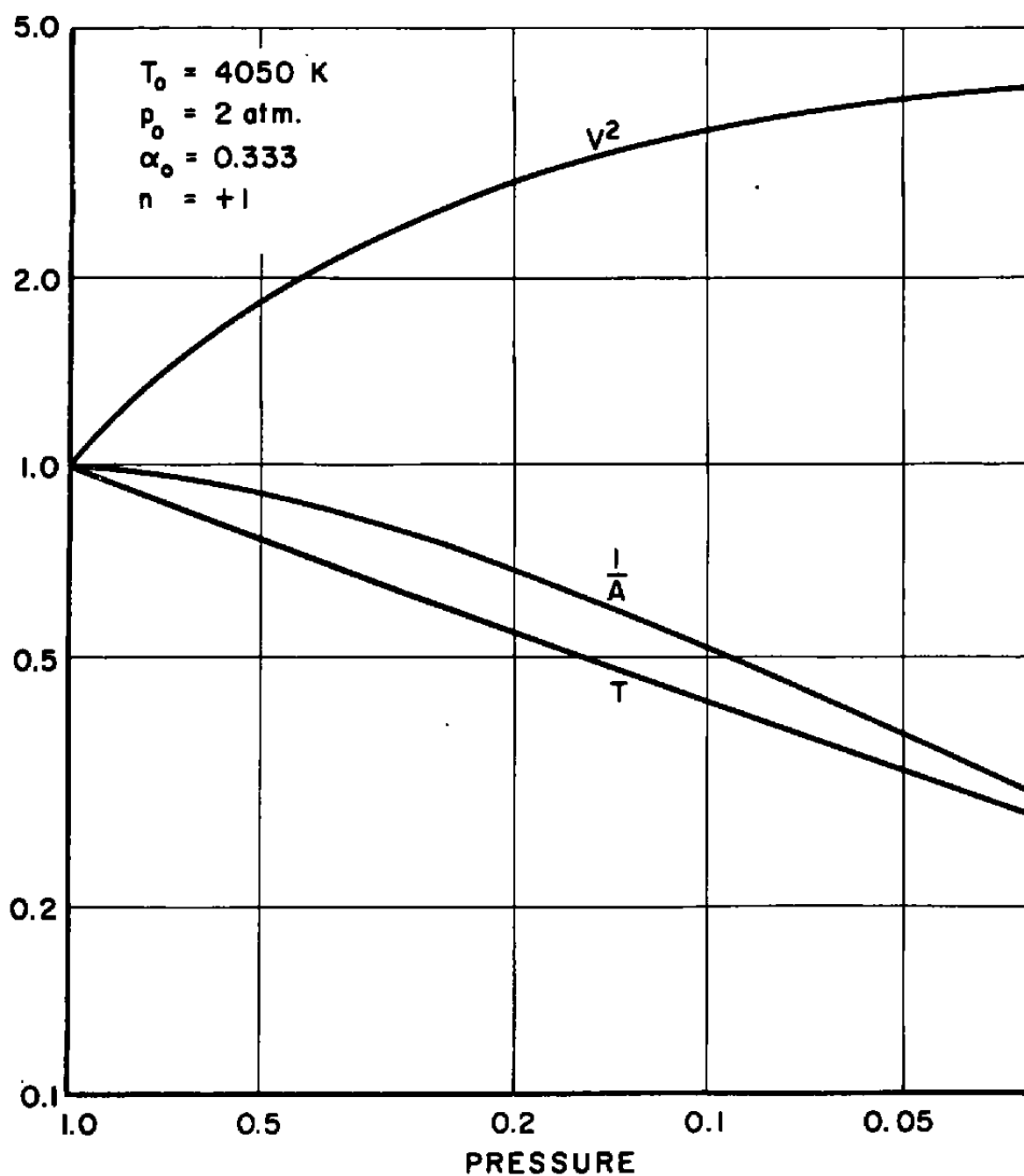
NOZZLE FLOW PARAMETERS, CASE III B

FIGURE E-14



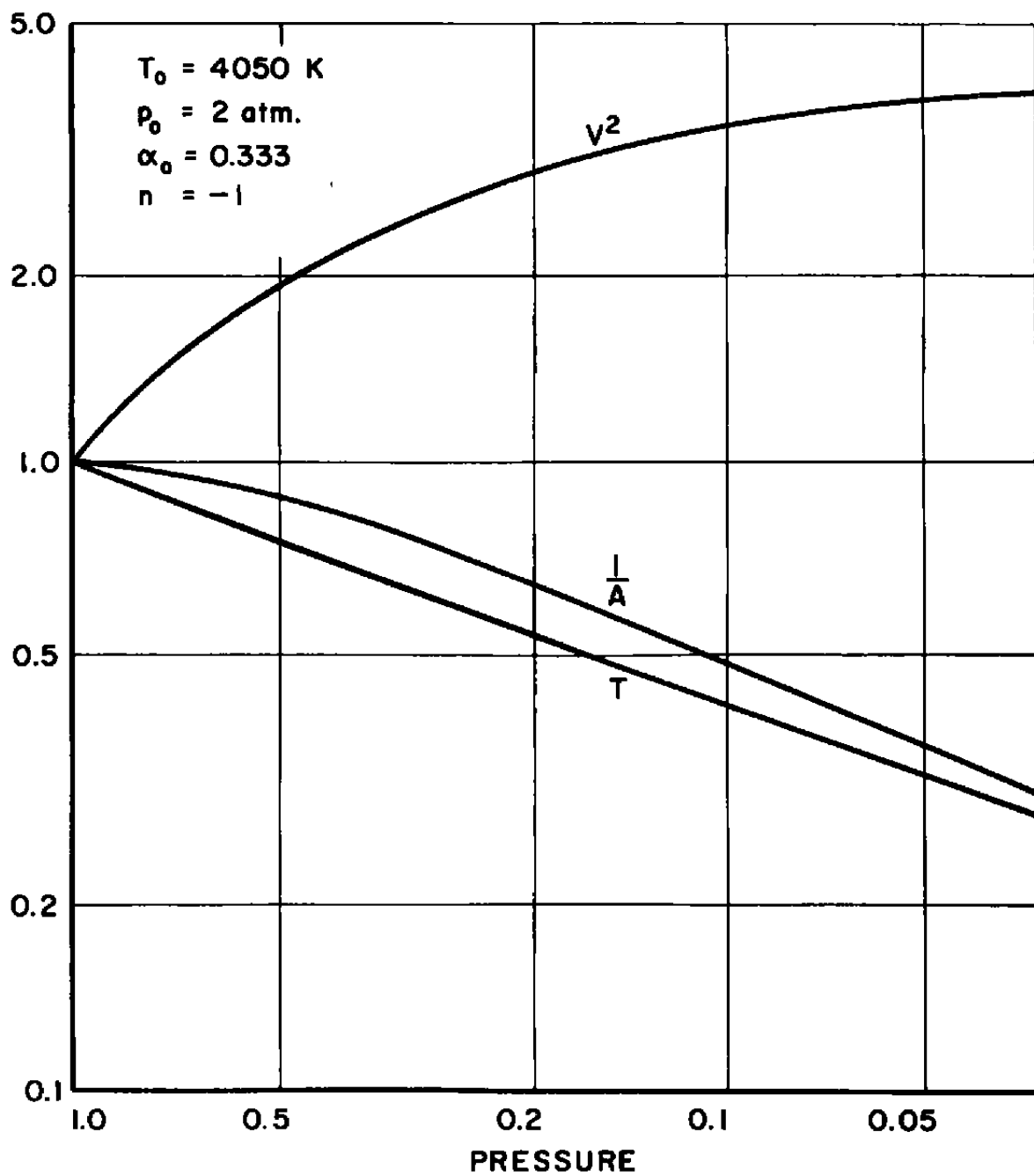
NOZZLE FLOW PARAMETERS, CASE III C

FIGURE E-15



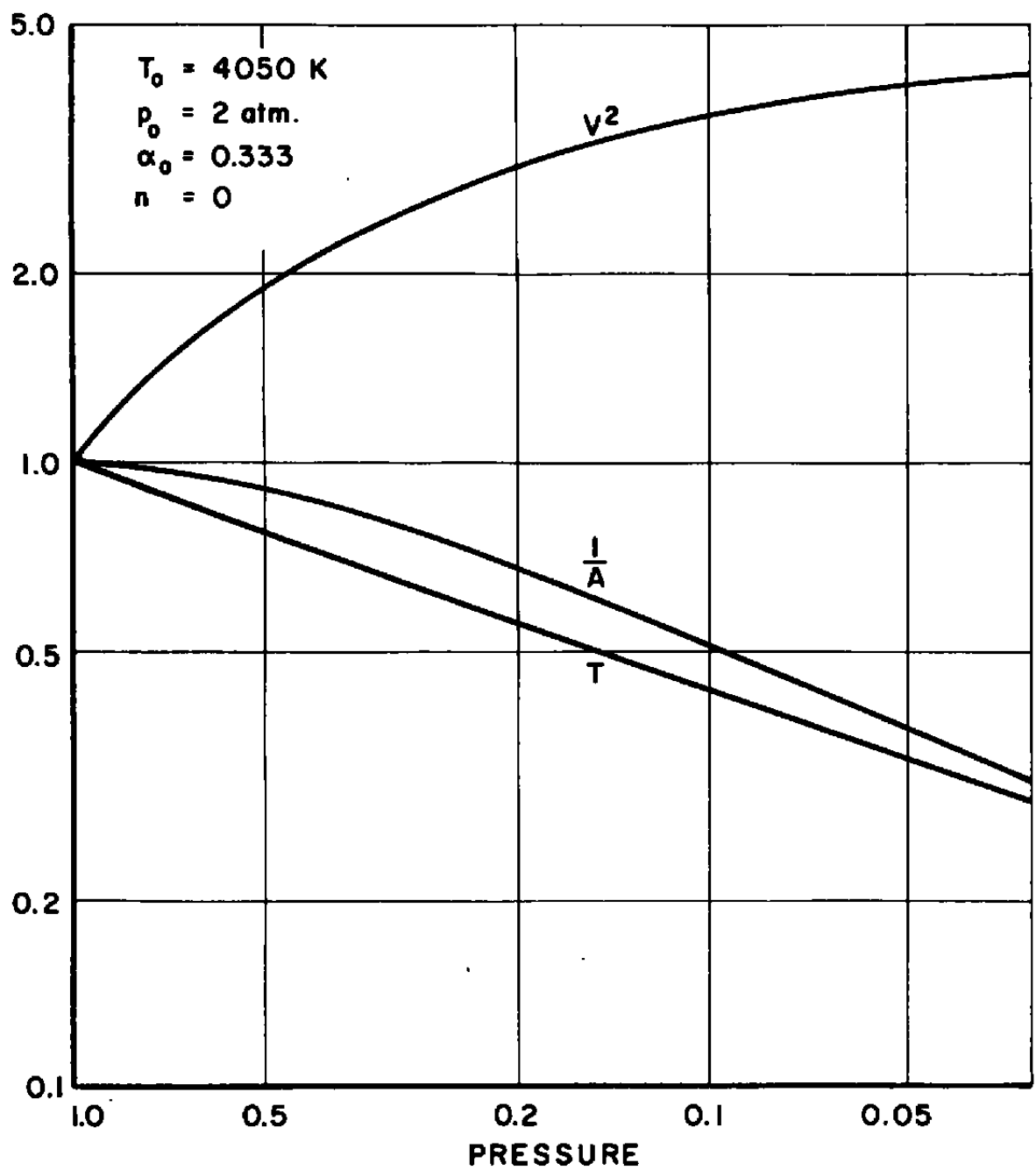
NOZZLE FLOW PARAMETERS, CASE III E

FIGURE E-16



NOZZLE FLOW PARAMETERS, CASE III F

FIGURE E-17



NOZZLE FLOW PARAMETERS, CASE III G

FIGURE E-18